CEREAL CHEMISTRY

Published bi-monthly by

The American Association of Cereal Chemists

W. F. GEDDES, Editor-in-Chief
R. J. TARLETON, Managing Editor } University Farm, St. Paul 1, Minn.
EUNICE R. BROWN, Editorial Asst.

Editorial Board: J. S. Andrews, G. Garnatz, Majel M. MacMasters, H. S. Olcott, Betty Sullivan, J. A. Shellenberger

CONTENTS

PAGE

The Quality of Flour Stored for Periods up to 27 Years. *E. N. Greer, C. R. Jones, and T. Moran* 439

Studies on the Effect of Drying Conditions upon the Composition and Suitability for Wet Milling of Artificially Dried Corn. *M. M. MacMasters, F. R. Earle, H. H. Hall, J. H. Ramser, and G. H. Dungan* 451

Influence of Storage without Aeration on the Microbial Populations of Rough Rice. *Dorothea J. Teunisson* 462

The Design, Construction, and Use of Micro Baking Equipment. *Merle D. Shogren and J. A. Shellenberger* 475

Program Control Attachment for Mixers Eliminating Human Errors. *Helen Baeder, Mary Kimball, and C. G. Harrel* 483

The Carbohydrates of the *Gramineae*. III. A Note on the Nature of Wheat Gum. *K. A. Gilles and F. Smith* 488

The Carbohydrates of the *Gramineae*. IV. Identification of the Sugars of the Flour of Wheat (*Triticum vulgare*). *R. Montgomery and F. Smith* 490

The Bread Staling Problem. Molecular Organization of Starch upon Aging of Concentrated Starch Gels at Various Moisture Levels. *N. N. Hellman, Barbara Fairchild, and F. R. Senti* 495

A Method for the Rapid Determination of Moisture in Doughs and Breads. *Howard W. Lincoln, B. M. Dirks, and C. G. Harrel* 506

Rapid Detection of Mercury on Cereal Grains. *D. K. Cunningham and J. A. Anderson* 513

Application of Amperometric Titration to the Determination of Potassium Bromate in Flour. *D. K. Cunningham and J. A. Anderson* 517

Book Reviews 522

Editorial Policy 529

Index to Volume XXXI 531

Entered as second class matter at the post office at Minneapolis, Minn., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized February 16, 1934. Published at 500 So. 5th St., Minneapolis, Minn.

Vol. 31 November, 1954 No. 6

The BAILEY #505-SS FERMENTATION CABINET

SHOWN AT THE DENVER CONVENTION

Model #505-SS

Walton Humidifier with constant level control

Stainless Exterior

Stainless Interior

Stainless or brass hardware

Built-in Sliding Shelf

110-120V 60C A.C. Current. Maximum load 1600 watts

¼ ton Refrigeration Unit
Extra – $280.00

Outside Cabinet Dimensions
60″ x 60″ x 24″ deep

Welded steel stand is 22″ high or will build to suit. Grey shrivel finish – stainless trim
Extra – $108.00

Model #505-SS Bailey Fermentation Cabinet – $1658.00
Est. Shipping Weight 1000 lbs.
Prices F.O.B. Lincoln, Nebr.

CEREAL CHEMISTS' EQUIPMENT MANUFACTURER

NATIONAL MFG. COMPANY
LINCOLN, NEBRASKA

FLOUR FOR MAN'S BREAD*

A Brief History of Milling and Baking by **SCIENCE WRITER**

CHAPTER III. *How Wheat Cultivation Migrated*

STARTED FROM ONE STRAIN

It is probable that all of today's varieties began with a single strain of wild grain. Very likely this was wild einkorn.

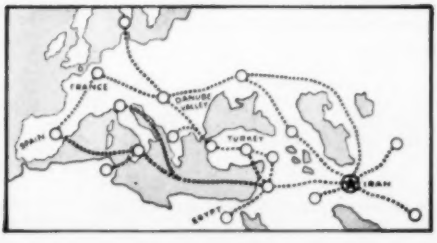
We know that this wheat was cultivated in Mesopotamia and central Asia Minor thousands of years ago. It was not a very satisfactory wheat, having a somewhat bitter taste and dark grains.

Another wheat, emmer, was widely cultivated in early agricultural days. Even today, it is found growing wild in Syria and Palestine and other places along the southern edge of the einkorn area. It must have been a popular grain because it has been discovered in early Egyptian settings and we know that it grew in the Danube Valley.

BREAD WHEATS DEVELOPED

The development of the bread wheats, caused either by matings with wild grasses or by an accidental doubling of the parent wheat's chromosomes, had an enormous influence on the spread of wheat-growing and milling. Most of these bread wheats have naked kernels and therefore are easier to mill. They have a better taste, too.

Fanning out from Iran where they probably originated, the bread wheats spread across Europe and Asia and into the Nile Valley in Africa. Einkorn and emmer had been introduced earlier into these places, and the bread wheats followed them. The migration of the naked kernel wheats began about 2100 B.C.



GRAIN EMPIRES FORMED

Great grain empires grew up in Egypt along the Nile and in Mesopotamia beside the Tigris and Euphrates. These rivers were used to irrigate the grain fields which were thus made extraordinarily productive. So important was wheat-culture to these areas that even religious beliefs were bound up with production of grain.

GRAINS GO ACROSS THE WORLD

During the Europeans' great period of colonizing beginning in the 1700's, wheat was carried to new lands in the temperate zones around the globe. It is interesting to note that today wheat-growing has been adapted to quite different climatic conditions from those under which it developed in the Near East.

VITAMINS AND WHITE FLOUR, WHITE BREAD

In the United States and Canada, as well as in other countries throughout the world, white flour and bread enrichment is an accomplished fact. In milling wheat to achieve the white flour which consumers demand, vitamins and minerals are unavoidably lost. Enrichment restores the following important nutrient factors: thiamine, riboflavin, niacin, and iron. Some processors add calcium, too. Enrichment thus provides better nutrition.

This is one of a series of articles which is being published in professional nutrition and dietetic journals, and which will be widely distributed for educational purposes. Reprints of this and all other chapters are available without charge. Write to the Vitamin Division, Hoffmann-La Roche Inc., Nutley 10, New Jersey. In Canada: Hoffmann-La Roche Ltd., 286 St. Paul Street, West; Montreal, Quebec.

*This is the title of a definitive history of milling by John Storck and Walter Dorwin Teague, published by the University of Minnesota Press at Minneapolis and copyrighted by the University of Minnesota. It is used with permission as a source of material for this series of advertisements.

The next chapter titled: "The Business of Milling Begins" will be published in the near future.

Enriched with vitamins and iron for better nutrition

The response has been most enthusiastic

to the recently published proposal for FARINOGRAPH recalibration and standardization of Farinograph curves.

In order to maintain such standardization over the years, the proposal is based upon a periodic exchange of the new, stainless steel mixing units.

It will enable all FARINOGRAPH users to make identical curves from a given flour. Thus it will be a tremendous step toward the attainment of a dependable language of flour characteristics—a goal we have never lost sight of since the beginning of physical flour testing methods.

The FARINOGRAPH curve is an important element in this "language" of flour characteristics. You do not have to *purchase* a FARINOGRAPH in order to use one. It is available on small monthly rental payments and you have the privilege of stopping these rental payments at any time and returning the instrument. Under these easy conditions—without financial risk to you—you cannot really afford *not* to have a FARINOGRAPH at your disposal all the time. We invite your inquiry.

BRABENDER CORPORATION Rochelle Park, N.J.

loaf after loaf

you can count on

Highest Uniformity

Uniformity of bakery products is vital to repeat bakery sales. That's why you should always use National's yeast products. They're tops in Uniformity.

NATIONAL YEAST CORPORATION

FRANK J. HALE, President

Executive Offices:	Eastern Division Office:	Western Division Office:
Chanin Building 122 East 42nd Street New York, N. Y.	45-54 37th Street Long Island City New York	Pure Oil Building 35 E. Wacker Drive Chicago, Ill.

•Plants: Belleville, N. J. • Crystal Lake, Ill.

You can order all these essential bakery products

National Bakers Compressed Yeast
National Active Dry Yeast
National Baking Powder
National Baking Cream
National Bakers Margarine

National Bakers Malt Syrup
National Bakers Dry Malt
National Enrichment Tablets
National Yeast Food
National Puff Paste

National 7-in-1
Armour Cloverbloom Frozen Whole Eggs
Armour Cloverbloom Frozen Egg Whites
Armour Cloverbloom Armtex
Armour Cloverbloom Sugared Yolks

Noted For Uniformity and Light Color

Your tests will confirm the quality of these Merck Vitamin Mixtures

In the mill or in the control laboratory, MERCK VITAMIN MIXTURES stand the most critical examination. They are light in color, uniform in feeding characteristics, and handle accurately in all types of equipment. Preferred for these advantages by hundreds of mills, MERCK VITAMIN MIXTURES are readily available from stocks strategically located at:

Atlanta, Ga.; Buffalo, N. Y.; Rahway, N. J.; St. Louis, Mo.; Dallas, Texas; Knoxville, Tenn.; Chicago, Ill.; Seattle, Wash.; Kansas City, Mo.; Los Angeles, Calif.; Oklahoma City, Okla.; Ogden, Utah; Denver, Colo.; Minneapolis, Minn.

Merck Vitamin Mixtures

FOR FLOUR ENRICHMENT

FIRST TO CONTAIN THIAMINE MONONITRATE

Research and Production for the Nation's Health

MERCK & CO., INC.
Manufacturing Chemists
RAHWAY, NEW JERSEY

© Merck & Co., Inc.

Sargent Constant Temperature Bath

The 0.01° C. Sargent Constant Temperature Water Bath, which is employed in many laboratories throughout the world where a precise, reliable thermostat is required, is now being supplied with an improved relay unit and heating system. The central heating and circulating unit of the bath is now equipped with three cylindrical heating elements rated at 200, 300 and 400 watts respectively. The 200 watt heater is controlled by the No. 81835 mercurial thermoregulator through a thyratron tube and saturable core reactor in the relay unit. (The use of a saturable core reactor obviates the difficulties commonly encountered with mechanical relaying systems such as pitted contacts, broken moving parts and freezing.) By means of a control mounted on the panel of the relay the output of this heater can be varied from the full 200 watts to approximately 60 watts, thus permitting such adjustment of the heater output that positive overshooting of the regulatory temperature is minimized. With the improved relay system this bath can be adjusted to a precision of ±.005° C. when operating in the vicinity of 25° C.

In addition, the relay unit is equipped with a master switch, a switch for each heater and a pilot light to indicate that the circuit to the 200 watt heater is closed.

Maximum power consumption 1100 watts.

S-84805 WATER BATH — Constant Temperature, 0.01° C., Sargent. Complete with Pyrex jar, 16 inches in diameter and 10 inches in height; central heating and circulating unit; constant level device; cooling coil; No. 81835 thermoregulator and relay unit with cord and plug for connection to standard outlets. For operation from 115 volt 50/60 cycle circuits **$275.00**

SARGENT

SCIENTIFIC LABORATORY INSTRUMENTS • APPARATUS • SUPPLIES • CHEMICALS

Catalog No. 100 Now Available

E. H. SARGENT & COMPANY, 4647 W. FOSTER AVE., CHICAGO 30, ILLINOIS
MICHIGAN DIVISION, 1959 EAST JEFFERSON STREET, DETROIT 7, MICHIGAN
SOUTHWESTERN DIVISION, 5915 PEELER STREET, DALLAS 19, TEXAS
SOUTHEASTERN DIVISION, 3125 SEVENTH AVE., N., BIRMINGHAM 4, ALA.

"WE'RE BUYING AUGUST FUTURES NOW... FOR OUR CUSTOMERS' SAKE"

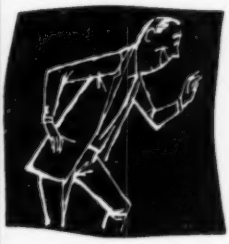
Old Timer: "Yup! We're buying August futures now, for the sake of our customers."

Upandcomer: "Really, Old Timer, aren't you blowing your cork on this one? There *are* no August futures."

Old Timer: "That's where you're wrong, Sonny. I'm talking about a mighty important August 'future'. . . I mean our *sales* of self-rising flour and corn meal *next* August when heat and humidity are putting the squeeze on shelf life and kitchen performance. I'm talking about a sure-fire 'hedge' against complaints and poor baking performance next summer."

Upandcomer: "Say! If you can make *that* kind of a hedge, it will take a lot of the risk out of next summer's production. But how are you going to control the weather?"

Old Timer: "That's just the point! No one can control the weather but we *can* do something to protect our brands. The best protection we can give our self-rising flour and corn meal is to contract for next summer's supply of V-90. Then we *know* our brands will have maximum shelf life and a kitchen performance that will bring customers back for more."



Upandcomer: "Is V-90 *really* that good?"

Old Timer: "Well . . . figure it out for yourself. We've been using V-90 for *15 years* and we've never had to worry over shelf life. *15 summers* have come and gone and our sales of self-rising flour and corn meal have shown a steady increase. That's why we're sure . . . *dead* sure . . . that V-90 will bring us through next summer. And that's why we're contracting for V-90. It's a sure-fire deal to protect August 'futures'. . . *next* August sales, that is!"

YOU'RE SAFE...YOU'RE SURE...WITH V-90®

THE PHOSPHATE CRYSTAL WITH A "RAIN COAT"*

*Coated Anhydrous Monocalcium Phosphate

VICTOR CHEMICAL WORKS

141 WEST JACKSON BOULEVARD • CHICAGO 4, ILLINOIS

Maryland mill installs new LABCONCO laboratory

D. A. STICKELL and Sons, Hagerstown, have stepped up control and research activities with their new LABCONCO feed laboratory. LABCONCO specialized steel furniture and apparatus save time, permit full operation with minimum staff.

Note safety dispensing stand (for acids and caustic) at far left. Carboys are stored in cabinet. Dangerous solutions are elevated by vacuum, dispensed over lead top table.

LABCONCO KJELDAHL apparatus (for protein determinations) is 12-unit hoodless combination model complete with water control and digestion timer. At right is LABCONCO illuminated titration table.

SIX-UNIT GOLDFISCH fat extractor (for fat and carotene determinations) sits on cabinet specially designed to speed this work.

GET THE FACTS on how LABCONCO apparatus and furniture cut laboratory costs. Write today for free illustrated booklet E-54. Describe what you are considering. You'll get helpful information by return mail. No obligation, of course.

Laboratory Construction Company

1115 Holmes Street **Kansas City, Missouri**

CEREAL CHEMISTRY

Vol. 31 November, 1954 No. 6

THE QUALITY OF FLOUR STORED FOR PERIODS UP TO 27 YEARS[1,2]

E. N. GREER, C. R. JONES, AND T. MORAN

ABSTRACT

At moisture contents of 13–14% flour in *non-gas-tight* tins generally became perceptibly rancid after about 5 years' storage at ordinary English temperatures (unrecorded but probably generally in the range 10°–20°C.); baking quality however remained satisfactory up to 10 years in flours below 0.6% in ash content and above 11% in protein content. Above 14% moisture content moldy taints were found.

The contents of *gas-tight* tins showed a trend towards zero oxygen content as the carbon dioxide content rose to a limiting value of about 9%. In cases where the oxygen content had fallen below 5% the flour was free from taint after 8 years' storage. Thus in *gas-tight* tins the storage life may be limited to about 8 years by rancidity development (the general baking quality remains satisfactory as in the case of non-gas-tight tins) but if the flour is also packed in an inert gas in such tins its storage life will evidently be still further increased.

The fat in the stored flours was generally extensively hydrolyzed. The quantity of extractable fat tended often to decrease on storage, the fall being associated with deterioration in baking quality. A pH value below 5.2, determined in dough made from stored flour, was associated with deterioration in baking quality.

The literature of flour storage is confusing. In the opinion of Saunders and co-workers (13), flour may be stored for as long as 14 years with little deterioration in baking quality; storage for 10 years under good conditions is regarded as quite safe. In contrast, Fisher *et al.* (4), found that flour from English wheat, kept in galvanized iron bins in these laboratories, became unfit for breadmaking in less than 2 years. Other workers have reported a much shorter storage life even in the case of flours from strong wheats. Thus McCalla *et al.* (10) state that long patent flours from hard wheats, initially at 13.5% moisture content, deteriorated significantly in baking quality within 3 months when stored at 16°–28°C. in sealed containers. When stored

[1] Manuscript received May 17, 1954.
[2] Contribution from The Research Association of British Flour Millers, Cereals Research Station, St. Albans, England.

in bags, improvement occurred up to 6 months but further storage was harmful. Sinclair and McCalla (14) found the keeping qualities of flours milled from wheats grown in one part of Canada to be superior to those of flours milled from the same types of wheat grown in another part with different soil, though repetition of the work in later seasons (10) failed to show similar differences.

It is remarkable that in none of these papers is there any reference to the development of rancidity during long periods of storage. Thus Saunders *et al.* (13) give detailed results of baking tests of flours stored for periods up to 14 years but make no mention of the odor or flavor of the bread.

Experiments on flour in canisters by Thomas (16) showed that at 30°C. flour of 14.5% or more moisture content has practically no storage life but flours of 13% moisture could be kept for about 6 months. Beyond this time they tended to develop a musty smell, though baking quality decreased only gradually; at 20°C. the storage life was 6, 18, and 24 months at 15.8, 14.5, and 13% moisture content respectively. Thomas (16) cites the work of Dienst who reported that a vacuum dried patent flour (moisture content not stated) was stored for 22 years without any deterioration in baking quality. No reference to the odor or taste of the bread was made. Thomas (16) cites also the work of Neumann who found that vacuum dried flours after 4 years in vacuo at 4.9% moisture content (temperature not stated) appeared satisfactory and had the color, flavor and odor of fresh white flour. Baking quality and flavor of the bread were normal.

Cuendet *et al.* (2) have recently found that marked falls in loaf volume occurred after the periods of storage of flour, at 37.8°C. (100°F.), shown below corresponding to the following moisture contents:

	Moisture Content, %	
	10	14
	weeks	*weeks*
Untreated patent flour	38	10
Whole wheat flour	26	3

The storage times required for the development of undesirable odors at 37.8°C. were inversely related to the degree of refinement and, in most instances, were increased as the moisture content at which the flours were stored was lowered. With patent flours, the periods required were:

Moisture content (%):	3	6	10	14
Period (weeks):	26	38	10	3

Flours treated with chlorine dioxide tended to develop off-odors sooner

than the corresponding untreated samples. Storage (of whole wheat flour) under nitrogen did not delay the development of objectionable odor.

According to Fine and Olsen (3) the development of rancid, tallowy odors in grain and grain products is a matter of general observation, but in their experiments on patent flour rancidity did not occur during a period of 3 years. The flour was stored at room temperature with a moisture content of 5.6%. Reduction of the moisture content to 2% or less led to the development of rancidity in 2 to 4 months. This latter result is in general agreement with the experiments of Halton and Fisher (6) who found that the absorption of oxygen by flour at 60°C., other than absorption due to fungal action etc., became progressively more rapid as the moisture content was reduced. The reason for this absorption of oxygen was considered to be oxidation of the flour fat.

Through the courtesy of Trinity House, London, and of the Scientific Adviser's Division, Ministry of Food, samples of flour were recently obtained which had been stored in tins at ordinary temperatures for periods ranging from 4 to 27 years. The composition of the gas in those tins which were gas-tight has been examined as well as the condition of the flours.

Materials and Methods

The tins, intended for emergency use in British lighthouses, were filled and sealed in various years from 1926 onwards, and had as far as is known since been kept at normal room temperatures (probably generally in the range 10°–20°C.) with no special storage precautions. Most of the containers were 8¾ in. square by about 4½ in. deep with a 6 in. opening, protected by a tagger plate (soldered-on apron) below which a press-in lid was fitted. The inside surfaces of even the oldest tins were found in good condition with no sign of rust or penetration of the metal. When leakages were found they were always at the seams, or round the tagger plate.

Except for the 4-year old tins, which contained 3½ lb., all the tins were filled with 7 lb. (3180 g.) of flour. Assuming a solid density of 1.42, the volume actually occupied by the 7 lb. of flour would be 2235 ml., and, since the capacity of the tins was 5620 ml. the free and intergranular space together would be 3385 ml. The 17-, 21-, and 22-year old tins measured 8¾ in. square by 3¾ in deep; the capacity was thus 4690 ml., the flour being more tightly packed. In these tins the free and intergranular space would be 2455 ml.

Naturally the results do not include "controls" in the form of ob-

servations on fresh flour and the history of the flours prior to packing is not known. The examination, therefore, was related to normal experience with fresh flour of types similar in protein and ash contents to the stored samples.

Moisture Content	was determined by heating 2 hours at 120°C.
Ash	was determined by incinerating a 5 g. sample overnight in a silica vessel at 600°C. and weighing the resulting ash.
Nitrogen	was determined by the Kjeldahl-Wilfarth-Gunning method (1), and converted to protein by the factor 5.7.
Fat	was determined by extraction with cold petroleum ether (B. P. 40°–60°C.), the solvent being percolated through a column of flour.
Peroxide Values	were determined by means of the "cold" method described by Lea (9).
Free Fatty Acid	as oleic acid, was determined by titration of the fatty extract, in boiling 1:1 benzene-alcohol, with dilute alcoholic sodium hydroxide solution.
pH	was determined by the method of Halton and Fisher (5).
Baking Tests	were made on a system using 4 hours' fermentation (including final proof) at 80°F. (26.7°C.) with 1.3% yeast and 1.8% salt.

Tests for Leaks in Tins and Gas Analysis. Tins described as having large leaks were those emitting bubbles when the sides were gently pressed under warm water. Those which failed to show bubbles under this test were pierced with a "stabber" which was operated within a rubber sleeve temporarily attached in an air-tight manner to the surface of the tin. The stabber was connected to a gas-collection system previously evacuated. The sample of gas was transferred by means of Hempel pipettes to a Van Slyke apparatus.

Carbon dioxide was determined by absorption in *N* sodium hydroxide solution, and oxygen by absorption in alkaline hydrosulphite solution according to the standard procedure recommended by Van Slyke (12). Determinations on each tin were made in duplicate.

After removal of the gas sample, a short copper tube was soldered over the hole pierced in the tin and connected, together with an adjustable manostat, to a source of compressed air. The tin was held under water while the air pressure was increased. Tins described as having small leaks usually showed streams of fine bubbles when the pressure was increased to 20 to 40 in. of water. Those described as air-tight held a pressure equivalent to 80 in. of water for several hours.

Results and Discussion

The results of the examination of the non-gas-tight tins are given in Tables I and II.

The ash and protein contents of the 8, 10, and 27 year old samples suggest all-Canadian flours of 73 to 75% extraction. The 4-6 year old

TABLE I

GAS COMPOSITION, AND MOISTURE CONTENTS AND ODORS, OF FLOURS OF VARIOUS AGES STORED IN LEAKING TINS

Ref. No.	Age	Leakage[a]	Date Filled[b]	No. of Tins Examd.	Moisture	Gas Composition[c]		Odor[d] (Flour)
						CO_2	O_2	
	Yrs.				%			
1	4	L	12/48	2	13.9 – 14.2			1
2	4	V.S	12/48	1	14.1	2.1	17.2	0
3	6	S	8/47	4	13.4 – 13.8	0.7	18.7	2
4	6	L	9/47	1	13.7	...	...	4
5	6	S	9/47	4	13.7 – 13.9	0.6 – 0.8	19.0 – 19.7	3
6	8	L }	1/45	2	13.5 – 13.8	...	...	1
7	8	S }	1/45	2	13.4 – 13.5	...	...	1
8	8	L }	1/45	5	14.1 – 15.0	...	...	M
9	8	S }	1/45	3	13.9 – 14.1	...	...	M
10	8	L/S	2/45	3	13.8 – 13.9	...	...	3
11	8	L	5/45	3	13.7 – 14.4	...	...	3
12	8	S	5/45	3	13.5 – 13.8	...	...	2
13	10	L	'43	1	14.1	...	...	M
14	10	V.S	'43	1	13.9	1.4	15.1	2
15	10	V.S	'38	1	13.7	1.5	14.6	3
16	12	L	4/41	12	11.7 – 13.5	0.2 – 0.4	20.1 – 20.5	3
17	12	S	4/41	2	11.6 – 12.0	...	...	3
18	12	V.S	4/41	2	11.8 – 12.0	1.1 – 1.8	10.3 – 16.7	3
19	14	L	9/39	1	14.2	...	...	4
20	14	S	9/39	7	12.9 – 13.7	0.1 – 0.4	20.4 – 20.7	4
21	14	V.S	9/39	2	13.1 – 13.9	0.5 – 1.2	19.2 – 20.1	4
22	17	S	'31	1	13.3	0.5	20.5	4
23	17	V.S	'31	1	13.6	4.0	17.0	2
24	21	V.S	'27	1	13.3	4.3	16.7	3
25	22	V.S	'26	1	12.9	0.9	20.1	4
26	22	S	'26	1	13.5	0.2	20.8	4
27	27	L	'26	1	14.1	...	...	1
28	27	S	'26	2	14.0 – 14.2	0.3	20.3	1

[a] L means large; S means small; V.S. means very small.
[b] Month and year.
[c] % by volume.
[d] 0 means free from odor; 1 means very slightly rancid; 2 means slightly rancid; 3 means rancid; 4 means very rancid; M means musty.
[e, f] Groups of samples respectively below and above 13.8% in moisture content.

flours were of lower grade or higher extraction. Their ash contents and visual appearance were similar to those of straight run flours of about 80% extraction: the samples however could not have consisted of National flour because the extraction rate was 85% when these tins were filled (December 1948 and September 1947). This, together with the magnitude of the protein contents, suggests that they were

TABLE II

LOAF VOLUME, PROTEIN, FAT, AND OTHER CHARACTERS, OF FLOURS OF VARIOUS AGES STORED IN LEAKING TINS

Ref. No.	Age	Flour Protein[a]	Ash	Loaf Volume[b]	pH of Dough	Odor[c] (Flour)	Flour Fat	
							Amount	F. F. A.
	Yrs.	%	%				%	%
1	4	13.5	0.53 – 0.55	92	5.2	1	0.92 – 1.03	58 – 59
2	4	13.5	0.55	92	5.2	0	0.93	59
3	6	13.2	0.58	88	...	2	1.11	74
4	6	13.7	0.62	78	...	4	0.90	66
5	6	13.8	0.61	78	...	3	0.82 – 0.93	69 – 72
6	8	13.4	0.48	80	...	1	...	...
7	8	13.3	0.46	80	...	1	...	...
8	8	12.7 – 13.5	0.46 – 0.49	80	4.7	M	0.51	79
9	8	...	...	...	...	M	...	...
10	8	...	...	...	...	3	...	...
11	8	12.7	0.44	...	...	3	0.41	70
12	8	13.2	0.44	90	...	2	...	...
13	10	12.9	0.50	98	5.3	M	0.88	78
14	10	12.8	0.52	100	5.3	2	0.91	78
15	10	11.2	0.42	92	5.7	3	0.85	22
16	12	9.4 – 11.5	0.43 – 0.52	75	...	3	0.67 – 0.89	48 – 67
17	12	10.3	0.55	...	...	3	0.62	59
18	12	10.6 – 11.7	0.46 – 0.49	75	...	3	0.83 – 0.86	50 – 54
19	14	9.2	0.42	...	...	4	0.33	22
20	14	8.1 – 9.9	0.44 – 0.48	75	5.0	4	0.46 – 0.63	23 – 54
21	14	8.1 – 9.7	0.43 – 0.50	71	4.9 – 5.1	4	0.46 – 0.49	30 – 54
22	17	9.9	0.45	70	4.9	4	0.46	68
23	17	...	0.43	70	4.4	2	0.39	62
24	21	9.5	0.46	85	5.2	3	0.65	65
25	22	8.9	0.50	90	5.2	4	0.72	66
26	22	9.8	0.49	65	5.0	4	0.31	70
27	27	12.8	0.48	94	...	1	1.01	70
28	27	12.8	0.49	94	5.4	1	0.87 – 1.00	71

[a] Analytical results are expressed on 14% moisture basis.
[b] Expressed as % of volume for a fresh flour of good baking quality. On this scale 100 is good, 90 is satisfactory, 80 rather small, and 70 poor.
[c] 0 means free from odor; 1 means very slightly rancid; 2 means slightly rancid; 3 means rancid; 4 means very rancid; M means musty.

Canadian-milled flours of rather low grade. The protein contents of the flours from 14 to 22 years old are normal for British milled grists in the period when they were milled, grists which contained relatively low proportions of Manitoba wheat; the ash contents of these flours indicate a grade not better than about 73% straight run. Ash contents of 0.5% may represent the balance of the straight run after removal of some patent flour.

Baking Quality. The samples with ash contents above 0.60% showed serious deterioration in crumb quality in 6 years. Otherwise the crumb character was satisfactory during storage up to 10 years. Beyond this time it was generally poor and dense with the exception of the samples of flour which were 27 years old, in which it was very good. It is noteworthy that the protein content of the 27-year old flours was higher by at least 1% than that of all other samples older than 10 years and that their loaf volume was well maintained. Most of the samples older than 10 years, which had relatively low protein contents, gave small loaves but samples Nos. 24 and 25 were exceptional in this respect.

Odor. In every case when the flour was free from any abnormal odor the corresponding bread was also free from any undesirable taste. Equally when the flours were slightly or very rancid the breads had a similar taste.

The two 27-year old tins were a complete anomaly. Although one of them leaked badly and the other slightly, the flours had only a very slight rancid smell while the breads were free from any undesirable taste. The volume and crumb texture were also very good in both cases. It is possible that the flours had been stored for the bulk of the 27 years under gas-tight conditions and that leaks had only developed shortly before they were opened *e.g.* on the journey from the lighthouse to the laboratories.

Otherwise Table I, together with the baking results already given, suggests that at a moisture content of 13–14% the first limit to the useful life of flour in non-air-tight tins is set by the development of a rancid smell and flavor, but that under temperate conditions flour would be expected to remain free from this defect for about 5 years. When the moisture content exceeds 14% the taints developed suggest mold or bacterial activity. In this connection it is of interest that Milner, Christensen, and Geddes (11) have shown that mold growth is extremely slow when the moisture content is below 14.5%.

The tins of greatest scientific interest are those which were gas-tight but unfortunately these were confined to the 6- and 8-year old samples. The data applying to these tins are set out in Table III. None of these samples showed visible evidence of mold or insect activity. Apart from consideration of odor, they were generally of satisfactory baking quality.

Changes in Gas Composition in Gas-Tight Tins. In the case of the slightly musty sample of the highest moisture content, much of the carbon dioxide may have been generated by microorganisms. Apart from this and also one of the 6-year old flours which is somewhat

anomalous, the results show consistently a trend towards zero oxygen content as the carbon dioxide content rises to a limiting value of about 9%. The difference between this and the stoichiometric value of 21% corresponds to the oxygen which remains held by oxidizable flour constituents.

The attainment of this limiting value of 9% in the period of 8 years would suggest a rate of "respiration" not less than 3×10^{-3} ml. carbon dioxide / 100 g. flour / 24 hours. Working (17) found the same figure at 35°C. for flour of unspecified moisture content; at 25°C. it was 1×10^{-3}. Fisher and Halton (6) however found that with flour of 15.5% moisture content stored in an air-tight container at 25°C., after an initial induction period of about 20 days, all the oxygen in the accompanying air was absorbed in about 15 days, with production of about half the corresponding quantity of carbon dioxide. This corresponds to a rate of respiration about 500 times greater than Working's figure for 25°C. On the other hand it is evident from Table III that certain of the flours in air-tight tins had "respired" much more slowly than the majority, the proportion of oxygen being still relatively high even after 6–8 years.

Odor of Flour in Gas-Tight Tins. Four of the twelve samples of Table III are recorded as being slightly rancid or slightly musty. Taste panels composed of "ordinary consumers" were far less discerning than the authors, particularly in detecting rancidity. The practical conclusion is that flour stored in gas-tight tins can remain in good condition and free from significant rancidity for about 8 years.

The four samples referred to were the only cases where the oxygen content remained above 5%. Irrespective of the explanation of the relatively slow respiration of these samples, this suggests that prolonged contact with an atmosphere containing more than 5% oxygen gives rise to a rancid flavor in flour (or to mustiness if the moisture content is about 14% or more). It would therefore be expected that the storage life of the flour packed in a gas-tight container would be greatly increased if, at the time of packing, the air in the container were replaced by an inert gas such as carbon dioxide or nitrogen. Other factors will of course be relevant including the strength of the flour, the time interval after milling, its moisture content and the temperature at which the containers are stored. The present work suggests that a moisture content of 13–13.5% will guarantee freedom from taints due to activity of microorganisms over a period of years, while other evidence suggests that if the moisture content is lowered much below this level the tendency for oxidative rancidity is increased. This latter would of course be obviated by storage in an at-

mosphere sensibly free from oxygen in which case it might be an advantage theoretically to store at a low moisture content to minimize other deteriorative changes. Under these circumstances flour should certainly keep in good condition for ten years and probably much longer.

Changes in Fat. The free fatty acid content of the fat, which in freshly milled flour is 5–10%, had increased very considerably. This tendency has long been known. Thus Hartmann (7) found a figure of 60–70% after 12 months' storage. Sullivan, Near, and Foley (15) also found that baking quality was only slightly impaired by the presence of free fatty acid in amounts corresponding to complete hydrolysis of the fat. This is also in accord with our observations. In storage experiments at 37.8°C. Cuendet *et al.* (2) found a rapid rise in the free fatty acids content of flour at 14% moisture content but the extent of the rise decreased with decreasing moisture content. At 3% moisture content there was virtually no change in fat acidity in 52 weeks. They found however that, at 37.8°C., decreases in loaf volume and development of fat acidity tended to proceed in step. Although recognizing that oxidative changes in lipids and other flour constituents also occur, it was suggested that the increases which occur in fat acidity of flours may serve as a fairly reliable index of the over-all changes taking place upon storage which influence baking quality. Their findings at 37.8°C. can hardly however be applicable to storage under cooler conditions (below 20°C.) for it seems clear from the evidence presented and cited in the present paper that while on the one hand extensive hydrolysis of flour fat occurs relatively rapidly irrespective of temperature, deterioration in baking quality on the other hand is very greatly retarded at lower temperatures. In short, under cool conditions flour may retain good baking quality long after extensive fat hydrolysis has occurred.

In a personal communication Geddes points out that the studies of Cuendet *et al.* (2) indicate that the significance of hydrolytic and oxidative changes in the lipids in relation to the decrease in breadmaking value at 37.8°C. appears to differ with the moisture content and length of the storage period. Thus, for example, while at 3% moisture content the fat acidity hardly increased at all, there was marked deterioration in baking quality of whole wheat flour after about 38 weeks' storage. Further experiments are being made in the Minnesota laboratory in which lipids extractable with diethyl ether have been removed from whole wheat flour and returned to it after subjection to varying degrees of hydrolysis and oxidation, the reconstituted flours being then stored at 37.8°C. and 10% moisture

content. Preliminary results indicate that hydrolysis of 10 and 30% of the lipids have little influence on loaf volume after storage for 3 months, even when the fatty acids were oxidized before returning them to the flour. When all the extracted lipids (2.5% of the flour) were hydrolyzed, however, the loaf volume was markedly lowered, especially when the fatty acids were oxidized.

Although the present data on pH are insufficient for generalization they suggest that a value in stored flour below 5.2 implies poor baking quality. A low pH value is also associated with a relatively low content of extractable fat.

Peroxide values carried out on the extracted fat gave no consistent correlation with the degree of rancidity observed in the flour indicating that the peroxides are unstable. Likewise the color of the extracted fat was unrelated. The fats were mostly clear yellow or clear pale yellow in appearance except in the case of the 12- and 14-year old flours. The fats from the latter were all opalescent and of varying intensities of yellowness: those from the 12-year old were brownish yellow and some were opalescent. The 27-year old flours, however, gave clear yellow fats.

TABLE III

ANALYTICAL DATA[a] ON 6 AND 8 YEAR OLD FLOURS STORED IN GAS-TIGHT TINS

Age	Protein	Moisture	Ash	CO_2[b]	O_2[b]	Odor	Fat	F. F. A.[c]
Yrs.	%	%	%	%	%		%	%
6	13.2	13.4	0.57	5.5	4.4	free	1.00	76
6	13.2	13.6	0.58	6.5	9.1	S. rancid	0.97	76
8	13.1	13.3	0.44	2.8	12.4	S. rancid	0.79	54
8	13.6	13.8	0.48	4.6	6.5	S. rancid	0.78	62
8	13.6	13.6	0.49	6.1	0.2	free	0.92	62
8	13.6	13.7	0.47	7.0	0.2	free	0.89	59
8	12.8	13.9	0.44	7.7	0.3	free	0.86	77
8	13.5	13.8	0.50	8.0	0.2	free	0.93	65
8	13.2	13.9	0.47	8.6	0.0	free	0.93	64
8	13.3	14.1	0.47	8.9	8.8	S. musty	0.74	69
8	13.3	13.8	0.47	9.1	0.0	free	0.88	66
8	13.3	14.0	0.47	9.6	0.2	free	0.92	68

[a] Protein, ash and fat contents are expressed on a 14% moisture basis. Each line refers to an individual tin.
[b] % by volume of head gas in tins.
[c] Free fatty acids expressed as percentage of total fat.

Tables II and III do not suggest that the development of rancidity is related to change in the quantity of extractable fat or in its content of free fatty acids. Most of the fats, from flours both in air-tight and leaking tins, were extensively hydrolyzed, irrespective of the presence

or absence of taint. Nor was this feature related to change in baking quality. It is however interesting to note the low level of extractable fat shown by many samples of 8 or more years' age. Our colleague, Dr. J. B. Hutchinson (8) has previously noted that with very old flours the petroleum ether extracts had lost the yellow color found in extracts from fresh flour and that much of the fatty material had become insoluble in petroleum ether; while some rancidity was carried in the petroleum ether extract, most remained in the extracted flour. Sinclair and McCalla (14) also found a decrease with storage in certain of the extractable lipoidal constituents of flour. Dr. Hutchinson further found that when fats from old flours whose baking quality had become spoiled were added to ordinary flour they reduced loaf volume and made the bread crumb closer in grain; in this respect they differed from fat from fresh flour which had no adverse effect and indeed sometimes gave slight improvement. At the same time the defatted old flour still retained some factor adverse to baking quality, irrespective of whether the defatted flour was baked as such or after addition of fresh fat. This factor, it was thought, might be an insoluble condensation product of the oxidized fatty acids. It appears from the present results that there is a general tendency for low percentages of petroleum ether extractable fat resulting from very long storage to be associated with severe deterioration in baking quality but the association is by no means clear cut.

Acknowledgments

We are indebted to our colleagues Dr. P. Halton, Dr. D. J. Cosgrove, and Mr. J. D. Campbell for their help in the experimental work.

Literature Cited

1. Association of Official Agricultural Chemists. Official methods of analysis (7th ed.). Assoc. Offic. Agr. Chemists: Washington, D.C. (1950), p. 13.
2. Culnedt, L. S., Larson, E., Norris, C. G., and Geddes, W. F. The influence of moisture content and other factors on the stability of wheat flours at 37.8°C. Cereal Chem. **31:** 362–389 (1954).
3. Fine, M. S., and Olsen, A. G. Tallowiness or rancidity in grain products. Ind. Eng. Chem. **20:** 652–654 (1928).
4. Fisher, E. A., Halton, P., and Carter, R. H. Studies on the storage of wheaten flour: I. The influence of storage on the chemical composition and baking quality of flour. Cereal Chem. **14:** 135–161 (1937).
5. Halton, P., and Fisher, E. A. Observations on the determination of hydrogen-ion concentration of dough, and on the relation of hydrogen-ion concentration to flour grade. Cereal Chem. **9:** 1–9 (1932).
6. Halton, P., and Fisher, E. A. Studies on the storage of wheaten flour: II. The absorption of oxygen by flour when stored under various conditions. Cereal Chem. **14:** 267–292 (1937).
7. Hartmann, W. Uber den Nachweis des Alters bei Mehlen. Z. Untersuch. Lebensm. **59:** 364–379 (1930).
8. Hutchinson, J. B. Unpublished work.

9. Lea, C. H. The determination of the peroxide values of edible fats and oils: the iodimetric method. J. Soc. Chem. Ind. (London) **65:** 286–291 (1946).
10. McCalla, A. G., McCaig, J. D., and Paul, A. D. Effect of various conditions of storage on baking quality of flour. Can. J. Research **17C:** 452–459 (1939).
11. Milner, M., Christensen, C. M., and Geddes, W. F. Grain storage studies. VI. Wheat respiration in relation to moisture content, mold growth, chemical deterioration, and heating. Cereal Chem. **24:** 182–199 (1947).
12. Peters, J. P., and Van Slyke, D. D. Quantitative Clinical Chemistry. Vol. 2. The Williams and Wilkins Company: Baltimore (1932) pp. 267–282.
13. Saunders, C. E., Nicholls, R. W., and Cowen, P. R. Researches in regard to wheat, flour and bread. Bul. No. 97. Can. Dept. Agr., Cereal Div. (1921).
14. Sinclair, A. T., and McCalla, A. G. The influence of lipoids on the quality and keeping properties of flour. Can. J. Research **15C:** 187–203 (1937).
15. Sullivan, Betty, Near, Cleo, and Foley, G. H. The role of the lipids in relato flour quality. Cereal Chem. **13:** 318–331 (1936).
16. Thomas, B. Die Trocknung von Mehl sur Erhohung seiner Haltbarkeit. Z. ges. Getreidew. **27:** 7–12 (1940).
17. Working, E. B. Measurement of respiration in flour. Cereal Chem. **13:** 234–236 (1936).

STUDIES ON THE EFFECT OF DRYING CONDITIONS UPON THE COMPOSITION AND SUITABILITY FOR WET MILLING OF ARTIFICIALLY DRIED CORN[1]

M. M. MacMasters,[2] F. R. Earle,[2] H. H. Hall,[2]
J. H. Ramser,[3] and G. H. Dungan[3]

ABSTRACT

Dent corn was harvested at 40, 30, and 20% moisture content, each, in 1950 and 1951. Each harvesting was divided into two lots, for drying at high and low relative humidity, respectively. At each relative humidity, samples were dried at approximately 120°, 130°, 140°, and 150° F. High sugar content was maintained in all artificially dried samples, in comparison with controls dried at room temperature. Niacin, pantothenic acid, riboflavin, and biotin contents of the samples were relatively unaffected by drying conditions. In 1950, but not in 1951, the pyridoxine content tended to be lowered by drying corn from an initial moisture content of 40% with air at 120° to 150° F. Laboratory processing for starch gave, in general, data which showed no clear correlation with drying conditions; however, corn dried at 150° F. tended to give poor processing results. Viability of the corn, as indicated by the 2,3,5-triphenyltetrazolium chloride color test, showed no correlation with over-all processing results. An unknown seasonal factor caused considerable differences between similarly dried samples of the 1950 and 1951 crops. This different response to drying conditions may have resulted from differences in the chemical or physical state of the kernel constituents, especially protein, which occurred because of differences in the growing seasons.

Artificially dried corn is becoming increasingly common on the commercial market. The preservation of soft, or high moisture, corn was formerly a relatively local problem in most years; only in unusual seasons was a considerable part of the crop picked at high moisture content. Generally the buyer did not have to take soft or artificially dried corn unless he was willing to do so. The increased use of the mechanical picker has changed the situation; in Illinois alone, pickers increased in number from 37,000 in 1945 to 67,000 in 1950 (2). Corn is picked mechanically at 20 to 25% moisture content, because picking losses are greatly increased if the corn is allowed to dry further in the field before harvest (2).

There is, in addition, a rapidly increasing trend toward the use of the picker-sheller, which also picks corn at high moisture content. Shelled corn packs more closely and allows less circulation of air through its bulk than does ear corn, hence the former dries more slowly in storage. Corn picked and shelled at 20 to 30% moisture content must be artificially dried for safe storage in any except very cold

[1] Manuscript received March 8, 1954.
[2] Northern Utilization Research Branch, Peoria, Illinois. One of the Branches of the Agricultural Research Service, U.S. Department of Agriculture.
[3] Illinois Agricultural Experiment Station, Urbana, Illinois.

weather; otherwise, the grain will mold and heat. Artificial drying of corn is, therefore, becoming increasingly common, and the trend will undoubtedly continue until most of the commercial corn crop is so handled in preparation for storage. Industrial users of corn, whether they process the grain for its chemical components or prepare it for food and feed uses, face a future in which they may have to operate chiefly, perhaps wholly, on artificially dried grain.

Several studies have been made to determine the effect of drying temperature upon the subsequent usefulness of the corn. In considering these, it is necessary to remember that it is the temperature of the corn itself which is important, not that of the air used for drying. Since it is difficult to measure the temperature within a grain kernel, it has generally been assumed that under the experimental conditions, the temperature of the corn comes into equilibrium with that of the drying air in cribs and bins. Shedd (8) stated that an air temperature of not over 130°F. should be used in drying corn destined for feeding or for wet milling. Experiments made by Hathaway *et al.* (5) indicated that the nutritive value of corn protein is adversely affected by temperatures of 140°F. or above, and that the energy value of corn is significantly reduced by drying the grain at or above 160°F. These workers recommended that corn be dried at not over 140°F. in order to preserve feeding value and market grade, and to avoid impairment of milling quality. Workers in the USDA (9, 10) have recommended temperatures between 95° and 135°F. for drying immature high moisture corn to maintain its feeding value.

In experiments on the drying of seed corn, Reed and Dungan (6) have shown that the factors to be considered in establishing "safe" drying practice are numerous and interrelated. Specification of temperature alone is not sufficient to cover all possibilities, although adherence to a temperature limit is often the practical approach to the problem.

The present study was undertaken to determine the effect of several variables, including initial moisture content of the corn, temperature, relative humidity and velocity of the drying air, and duration of the drying process, upon the composition of the dried corn and upon its suitability for wet milling for starch production. Results of preliminary studies made on 1949 crop year samples harvested at moisture contents up to 75% have been published elsewhere (4). Work is reported here on samples of the 1950 and 1951 crop years.

Materials and Methods

Illinois Hybrid No. 1277 yellow dent corn was field grown at the

Illinois Agricultural Experiment Station and harvested by hand as ear corn at approximately 40, 30, and 20% moisture content each year. Corn is usually considered to be mature at about 35% moisture content.

The ears were dried in the drier previously described (4) to a final moisture content of about 10 to 12%. One lot of corn at each initial moisture content was dried at each temperature with air at high and low relative humidity, respectively. Thus two lots of corn at each initial moisture content were dried at approximately 120°, 130°, 140°, and 150° F., respectively. A control was air-dried at room temperature from each initial moisture content. The corn was shelled at the Illinois Station.

Composition of the samples was determined by the methods used in the preliminary study (4).

The laboratory method used for separating starch from the samples was that previously described (4) except that scraping the gluten layer from the starch was repeated only twice, instead of four times. This change in procedure gave a better indication of differences in the ease of cleaning the starch.

The 2,3,5-triphenyltetrazolium chloride test has been described in detail elsewhere (1).

To obtain the annual rank classification shown in Table II, the samples of each year were arranged and numbered in order for each item considered, the lowest number being assigned for the best result, i.e., highest starch recovery, lowest protein in starch, highest protein in gluten, etc. The individual rank numbers obtained in the several lists were added for each sample to obtain the rank classification of the sample. The lower the rank classification, therefore, the better were the over-all processing results for the given sample.

Results and Discussion

The data obtained on the composition of the corn samples are summarized in Table I.

In both 1950 and 1951, drying corn from 40% initial moisture content with air at 120° to 150° F. tended to maintain high sugar content in comparison with that of the air-dried control, regardless of whether the relative humidity of the drying air was high or low. This difference tended to disappear as the corn matured to 30% and 20% moisture contents.

Ash, protein, and oil contents of the corn were relatively unaffected by the drying conditions. Possible changes in the nutritive value of the protein were not studied.

TABLE I

EFFECT OF DRYING CONDITIONS UPON COMPOSITION OF CORN

Drying Conditions					Composition of Corn (Moisture-free Basis)									
Initial Moisture	Temp.	R. H. of Air	Time	Velocity of Air	Starch	Total Sugars	Protein (Nx6.25)	Oil	Ash	Niacin	Pantothenic Acid	Riboflavin	Pyridoxine	Biotin
%	°F.	%	Hrs.	Ft./sec.	%	%	%	%	%	μg./g.	μg./g.	μg./g.	μg./g.	μg./g.
Dried from Approx. 40% Moisture Content														
1950														
42.0	149.7	38.7	46.5	1.66	69.6	3.74	10.6	5.2	1.52	26.4	9.5	1.8	2.6	0.04
40.2	151.1	11.7	24.5	1.84	70.3	2.72	10.6	5.3	1.50	25.7	9.0	2.0	2.8	.04
41.2	140.3	40.0	51.0	1.67	72.0	2.17	10.2	5.2	1.48	26.6	10.0	3.0	2.8	.03
42.0	140.3	10.4	28.0	1.79	70.4	2.94	10.8	5.3	1.46	28.5	7.5	1.9	2.5	.02
39.4	130.6	57.6	75.5	1.65	70.4	2.80	10.5	5.4	1.50	29.0	9.0	2.5	2.6	.05
38.5	130.5	9.8	33.0	1.84	70.7	3.49	10.8	5.2	1.45	25.7	9.0	1.6	3.3	.03
37.6	120.5	39.3	60.0	2.07	70.6	3.13	11.4	5.0	1.50	22.8	7.5	0.8	3.0	.07
38.2	120.1	16.0	39.5	1.83	70.7	3.37	10.9	5.0	1.45	20.5	7.7	1.9	3.1	.05
44.6		Air-dried control			71.0	1.72	10.9	4.5	1.59	26.5	10.5	1.4	4.6	0.06
1951														
39.8	150.0	39.5	44.5	3.93	71.8	2.26	9.5	4.9	1.40	28.5	7.3	1.9	4.8	0.07
37.0	149.3	10.0	23.5	4.29	71.0	3.86	9.3	5.1	1.45	29.6	6.4	1.8	5.2	.08
41.0	139.7	39.8	51.5	4.20	70.7	3.06	9.4	5.0	1.47	30.9	7.4	2.0	5.9	.06
36.7	139.9	9.9	26.0	4.34	70.3	3.96	9.4	5.1	1.38	29.2	6.8	1.6	4.7	.07
38.2	130.3	39.1	64.5	4.17	70.2	4.28	9.4	5.0	1.45	26.6	5.6	1.6	4.3	.06
39.0	129.4	10.4	38.5	4.34	71.4	4.06	9.1	4.9	1.44	30.0	5.6	0.8	4.0	.07
42.7	119.5	41.9	69.0	4.27	71.2	4.22	9.1	5.0	1.45	25.7	6.7	1.0	3.2	.08
36.3	119.8	15.0	31.5	4.37	71.9	3.66	9.8	5.0	1.45	26.4	6.8	1.0	5.1	.08
38.4		Air-dried control			71.8	2.33	9.6	4.6	1.53	30.4	5.8	1.5	5.9	0.08

(*Continued on next page*)

TABLE I—*Continued*

Drying Conditions					Composition of Corn (Moisture-free Basis)									
Initial Moisture	Temp.	R. H. of Air	Time	Velocity of Air	Starch	Total Sugars	Protein (Nx6.25)	Oil	Ash	Niacin	Pantothenic Acid	Riboflavin	Pyridoxine	Biotin
%	°F.	%	Hrs.	Ft./sec.	%	%	%	%	%	μg./g.	μg./g.	μg./g.	μg./g.	μg./g.
Dried from Approx. 30% Moisture Content														
1950														
29.8	150.0	37.9	30.0	2.17	72.1	2.32	10.6	5.0	1.49	25.5	9.0	1.9	3.8	0.05
31.1	150.4	9.7	21.5	1.94	72.9	1.77	10.9	5.0	1.50	26.9	9.5	1.9	3.5	.05
27.7	140.0	37.6	38.5	2.26	70.4	1.72	11.4	5.0	1.51	26.8	9.0	2.1	2.7	.06
32.6	139.6	9.4	23.5	1.99	71.6	1.84	10.4	5.0	1.49	23.6	9.0	1.8	3.8	.06
29.0	130.4	39.1	52.0	2.37	71.0	1.75	11.2	4.9	1.50	22.8	8.0	1.8	4.0	.03
31.2	129.5	10.1	24.0	2.06	71.4	2.22	10.4	5.1	1.49	26.2	8.0	2.0	3.1	.06
27.3	120.2	39.7	47.5	2.36	71.1	2.29	11.1	5.1	1.49	24.7	8.0	1.9	3.6	.05
30.5	119.1	13.1	31.0	1.97	70.7	2.42	10.8	4.9	1.50	22.5	8.0	2.1	3.4	.04
27.7		Air-dried control			71.1	1.85	11.0	4.7	1.43	26.0	9.5	2.2	4.6	0.07
1951														
25.4	149.3	40.0	31.0	4.13	71.6	2.91	8.9	4.8	1.45	28.7	5.1	1.9	5.4	0.06
28.1	149.5	10.5	23.0	4.16	73.3	2.85	9.6	5.0	1.55	29.8	5.5	1.7	6.4	.07
30.6	139.8	40.0	32.0	3.89	72.6	2.60	8.9	4.9	1.47	29.1	5.3	1.6	5.6	.07
28.0	139.5	11.0	23.0	4.02	71.0	2.68	9.4	5.2	1.46	30.5	7.0	1.6	5.5	.06
27.0	130.1	40.0	37.5	4.01	72.5	1.99	9.4	4.8	1.48	28.5	5.2	1.6	4.2	.08
30.2	129.9	15.9	24.5	3.94	71.8	2.88	9.6	4.8	1.50	28.4	6.8	1.5	4.8	.09
29.0	120.2	38.0	46.5	4.18	72.3	2.80	9.8	4.8	1.46	27.7	5.6	1.4	5.0	.08
32.2	119.5	17.7	29.5	3.94	71.5	3.42	9.7	4.9	1.44	26.1	6.2	1.6	5.6	.07
29.5		Air-dried control			72.6	2.60	9.4	4.7	1.47	29.4	6.5	1.0	4.7	0.08

(*Continued on next page*)

TABLE I—*Continued*

EFFECT OF DRYING CONDITIONS UPON COMPOSITION OF CORN

Drying Conditions					Composition of Corn (Moisture-free Basis)									
Initial Moisture	Temp.	R.H. of Air	Time	Velocity of Air	Starch	Total Sugars	Protein (Nx6.25)	Oil	Ash	Niacin	Pantothenic Acid	Riboflavin	Pyridoxine	Biotin
%	°F.	%	Hrs.	Ft./sec.	%	%	%	%	%	μg./g.	μg./g.	μg./g.	μg./g.	μg./g.
Dried from Approx. 20% Moisture Content														
1950														
20.2	150.3	36.7	23.0	2.61	72.4	1.66	10.7	4.8	1.45	25.5	8.5	1.6	4.0	0.08
20.6	147.0	11.0	13.0	2.16	71.5	1.86	10.3	5.2	1.48	25.1	9.5	1.8	3.6	.04
18.0	140.3	38.9	23.5	2.47	71.6	1.76	10.6	5.0	1.47	25.0	8.0	2.2	2.6	.05
22.4	140.6	10.1	12.5	2.27	71.0	1.84	10.8	4.9	1.49	23.3	8.5	1.8	3.5	.06
20.7	130.0	40.5	24.0	2.53	70.0	1.80	11.4	4.9	1.49	21.5	8.5	2.0	3.9	.05
22.0	130.8	11.3	16.5	2.23	71.8	1.68	10.8	5.0	1.48	22.7	9.5	1.9	3.9	.06
19.4	120.4	40.0	23.5	2.59	71.7	1.82	10.5	4.8	1.41	24.0	8.5	2.0	2.7	.05
19.8	119.5	12.2	16.0	2.39	71.6	2.04	10.3	5.0	1.46	25.0	8.0	1.9	3.5	.06
19.4		Air-dried control			70.3	1.92	11.1	4.8	1.51	26.4	9.5	2.3	4.2	0.07
1951														
19.6	149.7	40.0	23.0	3.93	72.6	2.63	9.1	4.8	1.44	28.0	5.6	1.8	6.0	0.08
18.6	149.7	10.0	12.0	3.91	71.9	2.63	9.2	4.9	1.48	30.6	6.2	1.5	3.5	.08
19.3	139.6	40.0	23.0	4.00	73.3	2.46	9.6	4.7	1.42	29.6	6.4	1.7	5.5	.07
21.0	139.9	10.0	13.0	3.89	72.8	2.65	9.1	4.7	1.46	25.4	7.5	1.5	9.9	.07
23.2	129.2	42.0	19.5	3.86	72.6	2.22	9.7	4.7	1.45	28.9	6.1	1.2	6.3	.08
21.0	129.8	10.0	14.0	3.82	73.0	2.70	9.1	4.7	1.49	25.0	5.5	1.3	6.0	.08
20.2	119.7	40.0	21.5	3.84	71.2	2.97	9.3	4.8	1.46	29.6	5.3	1.3	6.1	.10
20.4	119.6	15.0	14.5	3.79	72.8	3.01	9.2	4.7	1.46	28.4	6.1	1.4	5.3	.09
20.3		Air-dried control			71.9	3.04	9.1	4.8	1.48	29.3	5.9	1.3	7.0	0.08

In the 1950 samples, but not in those obtained in 1951, pyridoxine tended to be lowered by drying corn from an initial moisture content of 40% with air at 120° to 150° F. The niacin, pantothenic acid, riboflavin, and biotin contents of the samples were essentially unaffected by the drying conditions used in this study.

Data obtained from laboratory processing of the samples for starch are summarized in Table II. The results obtained with the 1951-crop-year samples did not confirm those obtained with the 1950-crop-year samples. In 1950, the samples dried from 40% initial moisture content processed best to give good recovery of starch of lower protein content than the rest of the series; the effect was most pronounced when air at low relative humidity was used for drying. In 1951, there was no clear correlation between processing results, as a whole, and any drying factor. In both years, corn dried at 150° F. tended to give poor processing results, while that dried at 140° F. gave the highest starch recovery, and, in one year, gave also the starch of lowest protein content.

Viability, as indicated by the 2,3,5-triphenyltetrazolium chloride test, was not correlated with over-all processing results. However, no attempt was made to simulate either degermination or gluten settling as practiced in industry; these steps are among those in which much difficulty has been reported in the industrial processing of artificially dried corn. It is probable that ease of degermination would be closely correlated with viability, inasmuch as dead germ is prone to undergo changes which render it less rubbery and therefore allow it to be more easily broken. Ease of gluten settling is usually correlated with the ease of separating starch and gluten during processing; it seems probable, therefore, that in cases where a high recovery of starch with low protein content was obtained good gluten settling could have been accomplished. On this basis, the 2,3,5-triphenyltetrazolium chloride test may give a partial indication of ease of processing (1) although the present data show several instances of poor correlation. The annual rank classifications showed no clear trends in effects of drying conditions.

It is evident from both analytical and processing data that the same variety of corn, grown and handled in the same way, differed in 1950 and 1951 with respect to effects of specific drying conditions. It is not kown what seasonal factor effected the difference. However, it was noted that in the 1950 series all of the separated starches contained relatively high amounts of protein, while in the 1951 series the protein content of the recovered starch was usually low. Previous work (3) indicated that difficulty in separation of starch and protein is com-

TABLE II

EFFECTS OF DRYING CONDITIONS ON VIABILITY AND LABORATORY PROCESSING OF CORN FOR STARCH

Drying conditions					Viability by T.T.C. test	Processing data (moisture-free basis)						Annual rank classification
Initial moisture	Temp.	R. H. of air	Time	Velocity of air		Starch recovery	Protein in starch	Starch in gluten	Protein in gluten	Starch in fiber	Protein in fiber	
%	°F.	%	Hrs.	Ft./sec.	%	%	%	%	%	%	%	Total points
Dried from Approx. 40% Moisture Content												
1950												
42.0	149.7	38.7	46.5	1.66	0	76.7	0.69	28.5	50.4	46.2	15.1	77
40.2	151.1	11.7	24.5	1.84	0	78.6	.44	35.9	46.2	38.6	11.9	48
41.2	140.3	40.0	51.0	1.67	0	80.7	.62	34.5	46.4	41.0	12.5	59
42.0	140.3	10.4	28.0	1.79	6	77.7	.50	35.6	47.6	39.6	12.6	43
39.4	130.6	57.6	75.5	1.65	0	79.4	.44	32.8	44.0	41.6	13.0	53
38.5	130.5	9.8	33.0	1.84	53	78.4	.50	32.6	50.8	38.2	10.2	25
37.6	120.5	39.3	60.0	2.07	70	73.4	.50	42.0	43.5	40.6	12.7	66
38.2	120.1	16.0	39.5	1.83	88	76.2	.50	40.6	42.6	39.6	10.9	51
44.6		Air-dried control			77	74.1	.56	39.8	46.1	44.1	17.6	71
1951												
39.8	150.0	39.5	44.5	3.93	0	72.3	0.50	36.2	48.2	45.7	11.2	67
37.0	149.3	10.0	23.5	4.29	0	68.6	.38	39.7	44.6	50.3	11.0	93
41.0	139.7	39.8	51.5	4.20	0	74.7	.50	32.5	50.5	46.5	11.5	54
36.7	139.9	9.9	26.0	4.34	0	66.6	.44	52.5	35.8	50.2	10.7	128
38.2	130.3	39.1	64.5	4.17	0	72.6	.38	32.6	46.7	47.9	11.0	49
39.0	129.4	10.4	38.5	4.34	15	67.6	.31	39.6	43.5	50.6	10.4	93
42.7	119.5	41.9	69.0	4.27	13	69.2	.31	33.2	46.3	52.0	10.8	74
36.3	119.8	15.0	31.5	4.37	85	69.3	.38	45.4	51.2	48.8	10.5	62
38.4		Air-dried control			97	65.1	.44	59.5	32.2	41.3	11.4	96

(*Continued on next page*)

TABLE II—*Continued*

Drying Conditions					Viability by T.T.C. Test	Processing data (moisture-free basis)						Annual rank classification
Initial Moisture	Temp.	R. H. of Air	Time	Velocity of Air		Starch recovery	Protein in starch	Starch in gluten	Protein in gluten	Starch in fiber	Protein in fiber	
%	°F.	%	*Hrs.*	*Ft./sec.*	%	%	%	%	%	%	%	*Total points*
					Dried from Approx. 30% Moisture Content							
					1950							
29.8	150.0	37.9	30.0	2.17	0	67.9	0.56	56.3	31.8	46.6	12.1	129
31.1	150.4	9.7	21.5	1.94	4	72.0	.62	41.5	46.5	41.4	12.5	82
27.7	140.0	37.6	38.5	2.26	11	75.0	.62	36.8	47.6	43.4	12.9	70
32.6	139.6	9.4	23.5	1.99	13	75.9	.69	46.8	41.3	45.3	12.0	106
29.0	130.4	39.1	52.0	2.37	46	72.0	.50	49.3	40.4	44.4	12.8	93
31.2	129.5	10.1	24.0	2.06	86	58.1	.69	38.7	46.5	42.0	10.9	80
27.3	120.2	39.7	47.5	2.36	84	71.6	.31	51.4	36.9	43.0	12.4	86
30.5	119.1	13.1	31.0	1.97	88	55.8	.62	46.0	42.1	42.5	14.1	96
27.7		Air-dried control			100	66.4	.50	61.8	30.1	45.6	11.3	103
					1951							
25.4	149.3	40.0	31.0	4.13	0	68.9	0.50	43.5	39.6	50.0	11.3	116
28.1	149.5	10.5	23.0	4.16	0	69.2	.44	32.8	45.7	47.4	11.2	71
30.6	139.8	40.0	32.0	3.89	0	68.6	.44	38.2	45.4	51.5	10.9	98
28.0	139.5	11.0	23.0	4.02	5	71.5	.50	37.3	47.5	49.4	10.9	83
27.0	130.1	40.0	37.5	4.01	14	70.2	.44	34.3	49.5	48.2	11.7	60
30.2	129.9	15.9	24.5	3.94	23	68.4	.50	44.5	41.3	49.5	10.9	113
29.0	120.2	38.0	46.5	4.18	69	70.2	.38	36.1	48.2	47.0	11.6	45
32.2	119.5	17.7	29.5	3.94	64	71.5	.38	47.3	36.4	48.5	11.1	80
29.5		Air-dried control			93	69.6	.31	52.6	35.2	45.0	10.8	75

(*Continued on next page*)

TABLE II—*Continued*

EFFECTS OF DRYING CONDITIONS ON VIABILITY AND LABORATORY PROCESSING OF CORN FOR STARCH

Drying Conditions					Viability by T.T.C. Test	Processing data (moisture-free basis)						Annual rank classification
Initial Moisture	Temp.	R. H. of Air	Time	Velocity of Air		Starch recovery	Protein in starch	Starch in gluten	Protein in gluten	Starch in fiber	Protein in fiber	
%	°F.	%	*Hrs.*	*Ft./sec.*	%	%	%	%	%	%	%	*Total points*
Dried from Approx. 20% Moisture Content												
1950												
20.2	150.3	36.7	23.0	2.61	3	64.7	0.62	58.1	32.2	47.8	12.1	137
20.6	147.0	11.0	13.0	2.16	10	73.0	.38	50.5	38.1	41.6	11.2	87
18.0	140.3	38.9	23.5	2.47	42	70.5	.88	43.5	42.8	44.4	11.4	110
22.4	140.6	10.1	12.5	2.27	7	76.4	.69	35.9	49.7	43.9	11.9	71
20.7	130.0	40.5	24.0	2.53	74	73.3	.56	41.9	42.6	42.8	11.7	80
22.0	130.8	11.3	16.5	2.23	41	74.1	.75	38.3	46.4	44.9	11.3	90
19.4	120.4	40.0	23.5	2.59	95	65.8	.56	62.4	28.8	44.9	11.4	111
19.8	119.5	12.2	16.0	2.39	91	74.6	1.12	40.3	45.8	44.7	11.1	86
19.4		Air-dried control			100	69.0	0.56	63.3	28.5	38.5	12.6	89
1951												
19.6	149.7	40.0	23.0	3.93	0	68.6	0.44	46.4	41.1	43.3	11.0	91
18.6	149.7	10.0	12.0	3.91	22	67.1	.44	52.0	36.9	49.2	11.2	115
19.3	139.6	40.0	23.0	4.00	34	67.7	.44	43.8	43.1	45.9	11.6	86
21.0	139.9	10.0	13.0	3.89	43	73.0	.44	35.0	46.2	48.2	10.7	53
23.2	129.2	42.0	19.5	3.86	28	69.9	.50	33.9	53.3	48.9	11.3	69
21.0	129.8	10.0	14.0	3.82	80	71.0	.38	40.2	44.0	50.2	10.8	72
20.2	119.7	40.0	21.5	3.84	90	69.7	.44	48.0	37.1	46.7	11.6	82
20.4	119.6	15.0	14.5	3.79	94	72.9	.38	40.0	44.9	45.3	10.4	42
20.3		Air-dried control			100	72.6	.44	48.8	38.9	40.2	11.0	61

mon when the corn is not quite mature. Shaw and Thom (7) recently pointed out that samples of corn at the same moisture level are not necessarily at the same state of maturity. It is probable that differences between the two sets of samples were the result of differences in chemical or physical state of the kernel constituents, especially protein which, in turn, resulted from differences in the growing seasons.

Final conclusions cannot be drawn from the data at hand. However, the data suggest that temperatures of 150° F. may have an adverse effect upon corn to be used for processing for starch production.

Acknowledgment

The authors gratefully acknowledge the aid of Mrs. Margaret M. Holzapfel who processed the corn samples and analyzed the resulting products; Miss Margaret C. Shekleton, who made the vitamin assays; and Mrs. Peggy D. Baird, who made the 2,3,5-triphenyltetrazolium chloride tests and assigned the rank classifications.

Literature Cited

1. Baird, Peggy D., MacMasters, Majel M., and Rist, C. E. Studies on a rapid test for the viability of corn for industrial use. Cereal Chem. **27:** 508–513 (1950).
2. Bateman, H. P., Pickard, G. E., and Bowers, W. Corn picker operation . . . to save corn and hands. Univ. Ill. Agr. Exten. Service Circ. **697:** 11 pp. (Aug. 1952).
3. Cox, Mary J., MacMasters, Majel M., and Rist, C. E. Laboratory processing studies on soft corn. Presented at the 32nd Annual Meeting of the Amer. Assoc. Cereal Chemists, May 19–23, 1947, Kansas City, Mo.
4. Gausman, H. W., Ramser, J. H., Dungan, G. H., Earle, F. R., MacMasters, Majel M., Hall, H. H., and Baird, Peggy D. Some effects of artificial drying of corn grain. Plant Physiol. **27:** 794–802 (1952).
5. Hathaway, I. L., Yung, F. D., and Kiesselbach, T. A. The effect of drying temperature upon the nutritive value and commercial grade of corn. J. Animal Sci. **11:** 430–440 (1952).
6. Reed, R. H., and Dungan, G. H. Drying hybrid seed corn. Univ. Ill. Agr. Exten. Service AEng **279:** 9 pp. (Oct. 1940).
7. Shaw, R. H., and Thom, H. C. S. On the phenology of field corn, silking to maturity. Agron. J. **43:** 541–546 (1951).
8. Sheedd, C. K., Sr. Mechanical drying of corn on the farm. U.S. Dept. Agr. Circ. No. **839:** 26 pp. (March 1950).
9. U. S. Bureau of Animal Industry. Feeding value of corn affected by drying temperature. *In* Report of the Chief of the Bureau of Animal Industry, Agricultural Research Administration, 1950. Report of the Administrator of Agricultural Research 1950, p. 151. U. S. Dept. Agr. 1951.
10. U. S. Bureau of Animal Industry. Feeding value of mature shelled corn not affected by drying temperature. *In* Report of the Chief of the Bureau of Animal Industry, 1951. Report of the Administrator of Agricultural Research 1951, p. 156. U. S. Dept. Agr. 1952.

INFLUENCE OF STORAGE WITHOUT AERATION ON THE MICROBIAL POPULATIONS OF ROUGH RICE[1]

DOROTHEA J. TEUNISSON[2]

ABSTRACT

Combine-harvested rice, air-dried to 14.3% moisture or less, contained moderate to large numbers of molds, aerobic bacteria, and anaerobic organisms; low to moderate numbers of actinomycetes; and relatively few yeasts.

Rice with 18 to 20% moisture, sealed in a glass-lined bin for 7 months in one trial and 34 days in another, became sour. Some molds survived but did not increase; aerobic bacteria survived or decreased in numbers; the facultative anaerobic organisms markedly increased; and the yeasts increased tremendously in most of the layers of the piles of rice. There was a loss in seed viability. Critical heating of the rice did not occur.

Other lots with 21.5 to 32.4% moisture, stored in sealed containers in the laboratory, showed the same general changes except that the aerobic organisms often increased.

The combine method of harvesting grain has resulted in increased production of rough rice at lower cost, but it has created problems of bulk handling and drying of moist grain (9). At maturity, rough rice in the field in the United States contains 20 to 30% moisture. Coomrod (4) has reported that maximum moisture content for safe storage, even temporarily, is probably 13 to 13.5%.

Rice often is combined faster than it can be processed in available driers, necessitating at least temporary storage of the moist grain, which can deteriorate quickly. On occasion, moist rough rice must be left on the trucks overnight or sometimes for a whole day before it can be dried. Under this condition the moist rice often sours.[3] This problem is particularly serious in warm and humid regions, where often the harvested seed becomes sour within a few hours. It is therefore desirable to find a method of storing rice without immediate drying.

Because sealed glass-lined bins have been used successfully in the Midwest for the storage of silage, this method of storing freshly combined rough rice was tested in 1949 and 1950, several agencies cooperating. It is thought that in this type of storage, all oxygen is eliminated by respiration of the stored material. Once substantially anaerobic conditions develop, little heating, loss in seed viability (7,

[1] Manuscript received March 8, 1954.

[2] Southern Regional Research Laboratory, New Orleans, Louisiana, one of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

[3] No statistics are available on the quantity of rice which is damaged in this manner.

8, 18, 20, 21), and suppression of mold growth would be expected. The procedure used and general results found have been reported (1, 2).

Since this laboratory was engaged in a program of fundamental research on the deterioration of rough rice during storage, advantage was taken of the opportunity to examine two lots of rice stored in a sealed bin. In addition, lots of freshly combined rough rice stored in sealed containers, and sound, air-dried, rough rice stored in paper bags and cartons were studied.

Storage Methods

Air-Dried Samples. Nine lots of freshly combined rice were air-dried in thin layers at Crowley, Louisiana, at the prevailing temperatures, between 17° and 37.8°C. (62.6° and 100°F.). They were then stored in paper bags or cartons for various periods, partly at Crowley at the temperatures just noted, and for the remainder of the time at this laboratory at 26° to 28°C.

One 100,000-bushel lot of Zenith, dried in a commercial drier, was stored for 7 months with periodic turning to cool the grain. Nevertheless, it had a history of heating. A sample of it was studied as soon as it was received in the laboratory.

Samples Stored in Sealed Containers. Seven lots of freshly combined rice of several varieties were stored in sealed containers to obtain sour rice. Some of the containers were jars with screw caps and others were 5-gal. cans with press-on lids. Four of these lots were air-dried after souring was noted, and stored in cartons until examined. The others were stored in the original closed containers until studied.

Sealed-Bin Storage. Two lots of freshly combined rough rice were stored at different times in a glass-lined bin described elsewhere (2). The first lot, 262 bbl. of Rexoro rice with a moisture content slightly higher than 18%, was put into the bin in one day, leaving a head space of about 4 ft. The bin was sealed and the rice was stored from November to May. The second lot of rice, 360 bbl. of Zenith with a moisture content of 19.3%, was put into the bin over a 42-hour period, beginning late one afternoon in October, leaving only 1 ft. of head space. The rice was stored for 34 days after sealing.

Bin Sampling. When the bin was opened from the top after both storage periods, samples of rice were taken from various levels in the piles and collected in sterile jars. Samples from the surface were scooped up with the jar, and those from beneath the surface were collected with a deep bin probe. Each of these samples was a composite of five loads from the same compartment of the probe. Samples were obtained from layers 1 ft., 2.5 ft., 5.5 ft., and 10 ft. from the top of

the pile of stored Rexoro rice. From the stored Zenith rice, samples were collected from the surface, 0.5 ft. below this, and from each subsequent foot from the top of the pile down with the exception of the eighth level from which no sample was obtained. Then the bottom of the bin was opened and samples were collected as the rice flowed out.

Analyses

Microbiological Analyses. These were made on seeds ground aseptically in an intermediate-type Wiley Mill[4] to pass a 20-mesh screen.

All the separate accessories for the mill which could be autoclaved or placed in an oven were sterilized by these methods. The mill itself was modified so that it could be rinsed with liquids. The modification will be described elsewhere. The inlet, grinding chamber, knife blades, and face of the mill were cleaned with Emulsept (800 p.p.m.), by means of small cellulose sponges held with forceps. The same parts were rinsed with sterile distilled water and then swabbed with 0.1% aqueous mercuric chloride, which was allowed to remain for 5 minutes. This was followed by rinsing with sterile distilled water until the wash water tested as low for chlorides as the distilled water blank. The mill was then dried with sterile cellulose sponges, using acetone. Preliminary experiments in which badly contaminated and sterile rice were ground alternately showed this method of sterilization to be satisfactory for the purposes intended.

Ten grams of the ground seed were mixed with 90 ml. of sterile distilled water in a sterile Waring Blendor cup for 1 minute. Serial dilutions of this suspension were plated for aerobic organisms in tryptone glucose agar (Difco), pH 7, and Waksman's agar, pH 4, as described by Skinner, Emmons, and Tsuchiya (24). To determine the presence of anaerobic organisms, tubes of melted tryptone glucose agar cooled to about 45°C. were each inoculated in duplicate with 1 ml. of the serial dilutions of the ground rice suspension, and mixed by rolling in a vertical position. The oxygen was removed from each tube with alkaline pyrogallol (25). Control tubes of methylene blue treated in the same manner remained colorless for 3 months. The cultures were incubated at 26°–28°C.

It is recognized that the method of preparing the rice suspensions for plating influences the number of colonies of microorganisms cultured and that the media used might limit the types of organisms isolated. While the rice is being ground and suspensions are being

[4] The use of trade names in this article is for identification and implies no endorsement of the manufacturer or the product.

made by the method reported, mold and yeast mycelia might be broken into segments, and clusters of mold spores, if any, might be separated to form individual colonies. Therefore, the counts of the molds and the yeasts which are dimorphic serve mostly as an index. However, the widespread differences between the samples would indicate that the grain was contaminated to different extents by molds and filamentous yeasts. The types of organisms isolated would be expected to be limited somewhat by any media that might be used. Waksman's agar was selected because of results obtained by Loeb and Mayne (16) with organisms from rice bran. They found that malt salt agar (5) and Waksman's agar gave the highest counts of molds and filamentous yeasts, but that the latter medium supported the growth of more varieties of molds.

Moisture and pH Analyses. Moisture contents were determined by drying whole rice in a forced-draft oven for 16 hours at 105°C. Determinations of pH were made with a Beckman meter on a sample of ground seed diluted 1:10 with sterile distilled water.

Germination Tests. The viability of the seeds was tested by the official method described by the Production and Marketing Administration (27), unless otherwise noted.

Results

Air-Dried Samples. The data on the air-dried rice are presented in Table I.

Germination of nine lots of air-dried rice stored in paper bags or cartons ranged between 80 and 93%. Germination of Zenith rice dried in the commercial drier was 70%.

Less than 1000 yeasts per g. were isolated from most of these samples. The molds usually occurred in a range of 10,000 to 90,000 per g. Actinomycetes were not usually found in the dilutions cultured; the few exceptions can be noted in Table I. The mesophilic aerobic bacteria occurred in millions per g. of rice. The organisms isolated under anaerobic conditions usually occurred in millions per g. of rice.

Samples Stored in Sealed Containers. Data on freshly combined rough rice stored in sealed containers to obtain sour seeds are given in Table II. The viability of these samples was not tested.

In these samples, which were sour, the yeast population was in the order of millions per g. compared to less than 1000 per g. in the control samples. Generally there was hardly any difference in the mold population of the soured rice as compared to the control samples, with one exception, noted in Table II. There was some increase in the actinomycetes in the soured rice over the control, but this was

TABLE I

DATA ON CONTROL SAMPLES OF ROUGH RICE AIR-DRIED AT PREVAILING ATMOSPHERIC TEMPERATURES AND IN A COMMERCIAL DRIER

Treatment and Variety	pH	Moisture Content[a]	Bacteria[b]	Molds[b]	Yeasts[b]	Actinomycetes[b]	Anaerobes[b]
		%					
Air-dried in thin layers at 17° to 37.8° C.[c]							
Zenith Lot 1, 49 days[d]	6.7	9.1	29,000	90	<1	<1	150
Zenith Lot 2, 21 days	7.0	10.8	39,000	24	360	<1	2,000
Rexoro Lot 1, 24 days	6.5	11.7	70,000	24	20	14	2,000
Rexoro Lot 2, 10 days	7.2	11.8	55,000	19	<1	<1	20,000
Rexoro Lot 3, 7 days	7.2	14.3	75,000	4,500	<1	<1	15,000
Selection No. 61-25-12[f], Lot 1, 28 days	6.9	11.9	292,000	19	<1	<1	2,000
Century-Patna, ? days	...[e]	...[e]	29,000	10	<1	<1	...[e]
Bluebonnet Lot 1, ? days	...[e]	...[e]	57,000	5	<1	<1	...[e]
Bluebonnet Lot 2, ? days	...[e]	...[e]	53,000	15	<1	<1	...[e]
Dried in commercial drier							
Zenith, C; 100,000 bu., 7 months in unsealed bin, turned periodically	7.3	11.2	1,000	18	1.5	1	1.2

[a] At time of microbial examination.
[b] Estimated numbers in thousands per g. of rice. Fifth day of incubation.
[c] Then stored in paper bags or cartons for the period noted.
[d] Composite of lot stored in the sealed bin.
[e] Not determined.
[f] See Reference No. 14 in Literature Cited.

TABLE II

DATA ON SEVEN DIVERSE LOTS OF FRESHLY COMBINED ROUGH RICE STORED IN SEALED CONTAINERS TO SOUR

Variety and Treatment of Rice	pH	Moisture Content[b]	Bacteria[c]	Molds[c]	Yeasts[c]	Actinomycetes[c]	Anaerobes[c]
		%					
Zenith Lot 2, m.c. 21.5%[a]							
12 days in 5-gal. can[d]	7.0	11.5	54,000	60	2,060	<1	18,000
Rexoro Lot 1, m.c. 24.3%							
7 days in 2-qt. jar[d]	6.9	10.5	228,000	36	4,000	<1	19,000
15 days in 2-qt. jar[d]	7.0	11.6	258,000	30	85,000	<1	20,000
Selection No. 61-25-12[e] Lot 1[e], m.c. 25.1%							
7 days in 5-gal. can[d]	6.8	10.4	42,000	50	10	<1	7,000
Selection No. 61-25-12[e] Lot 2, m.c. 32.4%							
40 days in pint jar. Numerous germinating seeds at jar walls	5.9	35.9	100	23	11,900	13	[f]
Rexoro Lot 2, m.c. 24.9%							
50 days in 5-gal. can							
"Molded" top layer	6.6	23.8	4,000	700	6,100	1500	24,000
Clean, free-flowing, central seeds	6.7	21.9	23,000	5	1,100	100	11,000
Rexoro Lot 3, m.c. 25.7%							
7 days in 2-qt. jar	6.9	25.1	280,000	6	190	<1	71,000
Rexoro Lot 4, m.c. not determined							
46 days in 2-qt. jar with loose cover	6.4	24.1	29,000	700,000	133,000	<1	15,000
46 days in 2-qt. jar with tight cover	6.7	21.7	226,000	16,000	89,000	10	100,000

[a] Moisture content (m.c.) at 0 hour of storage, by Steinlite method (see footnote 4 of text).
[b] By oven method at time of microbial examination.
[c] Estimated numbers in thousands per g. of rice. Fifth day of incubation.
[d] Then air-dried at 17° to 37.8°C. and stored in cartons.
[e] Described in Reference No. 14 in Literature Cited.
[f] Not determined.

confined to just a few samples. The aerobic bacteria generally survived in the soured rice and there was no change over that of the control samples. Anaerobic organisms (bacteria and yeasts) were present in slightly greater numbers than in the control samples.

Sealed-Bin Storage. Data, including results of germination tests, on seeds from various layers of the two lots of freshly combined, rough rice stored in the sealed bin are recorded in Table III.

There were two important changes in the microbial population after storage: 1) inhibition of mold growth and marked proliferation of yeasts, and 2) a noticeable difference in microbial population in surface layers as compared to deeper layers.

After storage, both lots contained millions of viable yeast cells per g. of rice in the top layer. This compares with the results found for rice which became sour in small sealed containers. The numbers of yeasts isolated in both aerobic and anaerobic cultures were lower at levels below 1 ft. from the surface of the piles, but even in deeper layers they were found in larger numbers than in the control samples. Filamentous yeasts were the most noticeable in the isolation medium. When young, these had the appearance of molds. The filamentous types are of interest because the rice appeared to be molded, especially in the top layer where seeds were matted and clumped. This same condition was found in many samples of freshly combined rice stored in sealed containers where the yeasts proliferated and the molds survived but did not increase. The types of yeast found are reported in detail elsewhere (26). They are *Endomycopsis chodati* (Nechitch) Wickerham & Burton, *Hansenula anomala* (Hansen) Sydow, *Pichia farinosa* (Lindner) Hansen, *Candida krusei* (Cast.) Berkout, *Oospora lactis* (Fres.) Sacc., and *Candida tropicalis* (Cast.). In two published reports concerning yeasts in stored seeds (6, 8), both of the types of yeast isolated are dimorphic, producing moldlike filaments under conditions of low oxygen tension, and in substrates of relatively low nutritional content (22, 28).

Molds were cultured only from the surface layer in rice stored 7 months. These were mostly dark green, sporulating strains and some Rhizopus-like growth. The incidence of only 600 molds per g. in this layer and less than 10 per g. in deeper layers appears significant, when these results are compared with those of the controls. Of the 90,000 molds per g. of Zenith rice prior to storage, approximately 40% were *Fusarium* sp. or spp., 25% were *Penicillium* sp. or spp., and 22% were *Aspergillus flavus-oryzae* group. *Stemphylium* sp., *Curvularia* sp., and *Rhizopus* sp. were present in smaller numbers. Only the predominant types survived 34 days' storage in the sealed bin.

TABLE III

DATA ON FRESHLY COMBINED ROUGH RICE STORED IN A SEALED, GLASS-LINED BIN

Variety	Storage Period	Depth in Pile of Rice	pH	Moisture	Bacteria[a]	Molds[a]	Yeasts[a]	Anaerobes[a]	Germination (14 days)
				%					%
Rexoro Lot 5[b, c]	7 months	Top	7.0	16.2	9,200	0.6	1,070	> 1,000	0
		1 ft.	6.7	19.0	5,200	<0.01	2,245	> 1,000	0
		2.5 ft.	6.8	18.1	345	<0.01	88	145	0
		5.5 ft.	6.9	17.3	31	<0.01	2	21	3
		10 ft.	6.9	18.3	230	<0.01	12	70	0
		Bottom	6.9	18.6	239	<0.01	18	120	2
Zenith Lot 1[d]	34 days	Top	5.1	27.6	Thousands	3.0	76,000	>100,000	39
		0.5 ft.	6.5	19.8	39,000	6.0	>15,000	> 36,000	64
		2 ft.	...	18.8	...	...	...	...	56
		3 ft.	...	18.4	...	...	...	...	15
		4 ft.	6.6	19.6	9,100	<0.1	2,400	> 18,000	5
		5 ft.	...	19.8	...	...	...	...	...
		6 ft.	6.5	18.9	530	<0.1	157	500	< 1
		7 ft.	6.6	19.5	2,200	0.5	420	3,000	< 1
		9 ft.	6.6	19.4	440	<0.1	134	600	39
		Bottom	6.6	19.6	3,900	2.5	280	800	87

[a] Estimated numbers in thousands per g. of rice. Fifth day of incubation.
[b] Viability tested by planting 100 to 400 seeds between double layers of moist paper toweling and incubating in a Minnesota Seed Germinator (Specialty Mfg. Co., St. Paul—see footnote 4 of text) at 26°–29°C.
[c] An air-dried sample of this lot was not available for study.
[d] Viability tested by the official method cited in the text.

Although reduced in numbers, *Fusarium* sp. or spp. survived in the greatest numbers in the top layers, and members of the *Aspergillus flavus-oryzae* groups were predominant in the bottom layer. *Penicillium* sp. or spp. survived only in the bottom layer where they were reduced from about 22,500 to only about 50 per g. of rice. Storage conditions were unfavorable for all types at the 4-, 6-, and 9-ft. levels of the pile. Types of molds found were among those isolated in 12 varieties of rice from Louisiana and Surinam by del Prado and Christensen (8). Fusaria are commonly found on rice in Louisiana, Japan, and the Philippines, according to Loh.[5]

Aerobic mesophilic bacteria in the top layers of both Rexoro and Zenith rice were at the same range of concentration as those usually found in the controls. The numbers decreased markedly in the deeper layers.

Actinomycetes were less than 1000 per g. in any parts of the sealed bins.

Yeasts were the predominant type of organisms isolated under anaerobic conditions from the rice stored 7 months. In that stored for 34 days, yeasts were also isolated in the highest dilution cultured anaerobically, but bacteria occurred in larger numbers. The bacteria were similar in morphology to those isolated aerobically.

When the bin was opened, the seeds had a sour odor. Wet areas were observed, particularly near the bin wall, after both storage periods. This region was probably the coolest part of the bin, particularly at night. Rice in the top layers was caked and moist, and covered with a white, powdery, microbial growth. For comparison, Fig. 1 shows a jar of laboratory-soured rough rice. These seeds have the same general appearance as those from the sealed bin, except that seeds in the lower part of the mass are cleaner. There are drops of water on the jar walls above the rice.

The moisture content of the seeds stored 7 months in the sealed bin did not change appreciably after storage, except in the top layer. Although some seeds in the top layer were noticeably wet when the bin was first opened (1, 2, 3), the moisture content of the seeds tested had changed from slightly above 18% to 16.2%. There was a slight variation from the original in moisture content of seeds in deeper layers. In Zenith rice stored 34 days in the sealed bin, moisture content of seeds in the surface layer increased from 19.3 to 27.6%. In deeper layers of this pile, moisture content of seeds varied only slightly from that before storage.

[5] Loh, Ta-Ching. A study of the pathogenicity and physiology of certain organisms of rice. Ph.D. thesis (unpublished). University of Minnesota.

Fig. 1. Freshly combined rough rice stored in a sealed jar for 46 days.

Distribution of moisture would not be expected to remain the same during storage. Semeniuk, Nagel, and Gilman (23) found a high moisture content of surface seeds in unsealed bins filled with fairly dry corn. They concluded that the most likely source would be condensation of water vapors from the atmosphere above and the corn below. Once mold development becomes established, higher moisture may be expected to develop as a by-product of mold activity. In the present experiment, development of bacteria and yeasts, not molds, would probably be responsible. Del Prado and Christensen (8) found that the moisture content of four samples of rice stored in sealed bottles was somewhat higher at the conclusion than at the beginning of the storage period.

There was no significant change in pH of seeds during storage, except in the surface layer of Zenith where the moisture content had increased to 27.6%.

As recorded in Table II, after 7 months' storage, the rice was no longer viable. After 34 days of storage, seed viability decreased in all layers except at the bottom of the bin. Viability varied in the other layers, but the decrease was marked at the 3- and 4-ft. levels, and loss was complete at the 6- and 7-ft. levels. A loss in viability in moist seeds stored in sealed containers has been reported by many investigators (7, 8, 18, 20, 21).

Milling quality of both lots of stored rice was relatively good, but the grade of the milled rice was poor because of the sour odor and discoloration of kernels (3).

As already reported (1, 2, 3), there was no critical heating such as usually would occur in moist rice stored in an unsealed bin. Daily temperature readings were reported at ten points in the bin.The rice did not heat above 32.8°C. (91°F.) during either storage period, but temperatures were as high as 35° to 38.9°C. (95° to 102°F.) in the air space above the grain.

At the end of the 7-month storage period, the concentration of carbon dioxide was 21.4%. In the 34-day experiment, all of the oxygen in all locations tested, except in the air space above the rice, was replaced by carbon dioxide after 2 days of sealed storage. By the third day, conditions were anaerobic throughout the bin.

Discussion

Proliferation of yeasts probably was influenced by high concentration of carbon dioxide, which developed during storage, and by low oxygen content, as was demonstrated in the sealed-bin experiments. Molds would not be expected to multiply in this atmosphere.

The occurrence of larger microbial populations in surface layers of the piles was probably due to two factors: 1) availability of oxygen for a longer time there than in the deeper layers and 2) translocation of moisture to upper layers. It was shown in the 34-day experiment that oxygen in the 1-ft. head space was not depleted until the third day of storage. It is probable that conditions became anaerobic more slowly in the first storage period (7 months) when there was a head space of 4 ft. Translocation of moisture is common in bulk storage of grain, and an actual increase in moisture in the surface layers was demonstrated (Table III). A subsequent increase in relative humidity (R. H.) in the interseed atmosphere at the surface probably resulted. According to the results of other studies (10, 12, 15), the R. H. of interseed atmosphere at the surface of the sealed bin must have been 90% or higher. Some molds can grow on rice in an atmosphere having R. H. as low as 65% (13, 19) and yeasts can grow at 80–90% (17), but it is

usually considered that bacteria cannot grow unless it is at least 95% (18, 20), which probably occurred in the visibly wet surface areas.

Temperatures in the seeds (32.8°C.) and in the air above the rice (39.9°C.) are above the optimum for yeasts, many of which cannot grow at 37°C. Loss in seed viability would be expected to enhance microbial growth in areas where other conditions were favorable (18, 21).

The souring in the rice stored for 7 days or longer, under anaerobic conditions, apparently is similar to the souring of other grain that has been reported. According to Easter (11), grain that is left wet for protracted periods is attacked by yeasts and bacteria and becomes "sour." Christensen and Gordon (6) found that a yeastlike organism, *Monilia albicans*, shown to be a facultative anaerobe, predominated in 7 of 15 commercial lots of corn studied in one year. It gave a decidedly sour and unpleasant yeasty odor to the corn.

The results of the present study suggest that rice "souring" is due to insufficient aeration and that proliferation of yeasts and survival of bacteria are associated with souring under the experimental conditions reported.

Further work is required on storage of freshly combined rough rice under controlled humidity and varying oxygen tensions to establish the relationship between the phenomenon of souring, anaerobic respiration of seeds, and microbial populations.

Acknowledgments

The rice was collected and samples prepared and supplied for this study by Vernon H. McFarlane. The author is grateful to him for his advice; to Aaron M. Altschul for his encouragement and help during this investigation and for his criticisms and helpful suggestions in the preparation of the manuscript; to Ruth Y. Mayne for identifying the molds; to Taylor H. McLemore for testing the viability of the seeds; to the personnel of the Louisiana State University Rice Experiment Station in Crowley, Louisiana, for furnishing samples of rice of known history; and to Clyde M. Christensen for his helpful suggestions on the manuscript.

Literature Cited

1. Anon. Rice storage experiment in progress in Louisiana. Rice J. **53**: 25–26 (1950).
2. Anon. "Glass bin" opened at Crowley. Rice J. **53**: 25–26, 28 (1950).
3. Barr, H. T., and Coonrod, L. G. Bulk drying and storage of rice on the farm. Agr. Eng. **33**: 158, 160, 162, 164 (1952).
4. Coonrod, L. G. Drying and storage of rough rice (in Southwest Louisiana). Rice Annual, p. 28 (1952).
5. Christensen, C. M. The quantitative determination of molds in flour. Cereal Chem. **23**: 322–329 (1946).
6. Christensen, C. M., and Gordon, Dorothy R. The mold flora of stored wheat and corn and its relation to heating of moist grain. Cereal Chem. **25**: 40–51 (1948).
7. Crocker, William, and Barton, Lela V. Physiology of seeds. Chronica Botanica Co.: Waltham, Mass. (1953).

8. Del Prado, F. A., and Christensen, C. M. Grain storage studies. XII. The fungus flora of stored rice seed. Cereal Chem. **29:** 456–462 (1952).
9. Efferson, J. N. The production and marketing of rice. Rice J. (1952).
10. Fenton, F. C. Storage of grain sorghums. Agr. Eng. **22:** 185–188 (1941).
11. Food and Agriculture Organization, United Nations. S. S. Easter, ed. Preservation of grains in storage. Studies, No. 2 (1948).
12. Gallaher, G. L. A method of determining the latent heat of agricultural crops. Agr. Eng. **32:** 34, 38 (1951).
13. Ghosh, J. J. Studies on the nutritional requirements of rice-inhabiting fungi. Science and Culture **17:** 135–136 (1951).
14. Jodon, N. E., and De La Houssaye, D. A. Rice varieties for Louisiana. La. Agr. Expt. Sta. Bull. 436 (1949).
15. Karon, M. L., and Adams, Mabelle E. Hygroscopic equilibrium of rice and rice fractions. Cereal Chem. **26:** 1–12 (1949).
16. Loeb, Josephine R., and Mayne, Ruth Y. Effect of moisture on the microflora and formation of free fatty acids in rice bran. Cereal Chem. **29:** 163–175 (1952).
17. Milner, Max. Biological factors in damp grain deterioration. Food Technol. **5:** 25–30 (1951).
18. Milner, Max, and Geddes, W. F. Grain storage studies. II. The effect of aeration, temperature, and time on the respiration of soybeans containing excessive moisture. Cereal Chem. **22:** 484–501 (1945).
19. Milner, Max, and Geddes, W. F. Grain storage studies. III. The relation between moisture content, mold growth, and respiration of soybeans. Cereal Chem. **23:** 225–247 (1946).
20. Milner, Max, Christensen, C. M., and Geddes, W. F. Grain storage studies. V. Chemical and microbiological studies on "sick" wheat. Cereal Chem. **24:** 23–38 (1947).
21. Oxley, T. A. The scientific principles of grain storage. Northern Pub. Co.: Liverpool (1948).
22. Scherr, G. H., and Weaver, R. H. The dimorphism phenomenon in yeasts. Bacteriol. Revs. **17:** 51–92 (1953).
23. Semeniuk, G., Nagel, C. M., and Gilman, J. C. Observations on mold development and on deterioration in stored yellow dent shelled corn. Iowa Agr. Expt. Sta. Research Bull. 349 (1947).
24. Skinner, C. E., Emmons, C. W., and Tsuchiya, H. H. Henrici's Molds, Yeasts, and Actinomycetes (2nd ed.), p. 50. John Wiley & Sons, Inc.: New York (1947).
25. Society of American Bacteriologists, Committee on Bacteriological Technic. Manual of methods for pure culture study of bacteria (4th ed.). Leaflet II, 4, 9 (1953).
26. Teunisson, Dorothea J. Yeasts from freshly combined rough rice stored in a sealed bin. Appl. Microbiol. **2:** 215–220 (1954).
27. U. S. Department of Agriculture, Production and Marketing Administration. Rules and regulations under the Federal Seed Act. Service and Regulatory Announcements No. 156 (March 1940; rev. July 1950).
28. Wickerham, L. J., and Rettger, L. F. A taxonomic study of *Monilia albicans* with special emphasis on morphology and morphological variation. J. Trop. Med. Hyg. **42:** 174–177, 187–192, 204–216 (1939).

THE DESIGN, CONSTRUCTION, AND USE OF MICRO BAKING EQUIPMENT[1]

MERLE D. SHOGREN AND J. A. SHELLENBERGER

ABSTRACT

Micro baking equipment for routine use was designed and constructed. The equipment included dough mixer, oven, fermentation cabinet, sheeting rolls, molder, bread pans, and loaf volume meter. Farinograph curves were obtained using 10 g. of flour. Doughs weighing approximately 13 g. were mixed, fermented, and baked with satisfactory results compared with the standard A.A.C.C. method.

The rapid development of micro methods of analysis during the past half-century and the extensive use of such methods in chemical laboratories has resulted in the application of some of these methods to cereal technology. Micro milling and analytical technics have been proposed by several workers (5, 7, 9). Werner (12) reported that the first widespread interest and recognition of the potentialities of a miniature baking test resulted from the publication in 1903 of the book by Maurizio entitled "Getreide, Mehl und Brot." According to Van Scoyk (11), the credit for awakening cereal chemists to the possibilities of precision operation of a baking test using 100 g. of flour and of experimenting with the use of 25-g. flour doughs belongs to Werner (12). Micro baking technics have been developed and used by Geddes and Aitken (6), Van Scoyk (11), and Harris and Sanderson (8).

The object of this research was to design equipment and develop laboratory procedures satisfactory for the routine testing of large numbers of samples when no more than 100 g. of wheat are available. With this quantity, moisture, protein, ash, flour yield, absorption, mixing time, and loaf volume can be determined.

Materials and Methods

Equipment designed and constructed included a dough mixer, fermentation cabinet, sheeting rolls, molder, oven, loaf volume meter, bread pans, and 10-g. farinograph bowl.

Micro Dough Mixer. A mixer similar but slightly smaller than that used by Finney, Morris, and Yamazaki (4) for the micro cookie test was constructed by the National Manufacturing Company, Lincoln, Nebraska (Fig. 1.). The mixing action is similar to that of the record-

[1]Manuscript received May 24, 1954. Contribution No. 249, Department of Flour and Feed Milling Industries, Kansas Agricultural Experiment Station, Manhattan. Presented at the Annual Meeting of the American Association of Cereal Chemists held at Denver, Colorado, May 23-27, 1954.

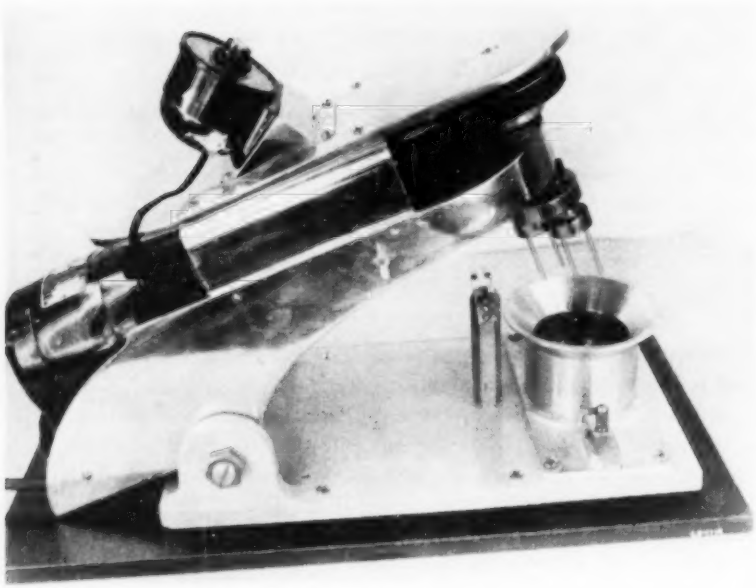


Fig. 1. Micro dough mixer.

ing dough mixer. The mixer differs in having but two pins in a smaller bowl. The micro mixer is capable of mixing doughs made from as little as 8 g. of flour.

Fermentation Cabinet. The fermentation cabinet was also made by the National Manufacturing Co. and is smiliar in design to the Bailey cabinet manufactured by them except that it is about one-third as large. The outside dimensions are 29¼ in. wide, 24 in. deep, and 64½ in. high. The cabinet door openings are 10½ in. high and 13½ in. wide.

Sheeting Rolls and Molder. The sheeting rolls and molder were combined into one machine as illustrated in Figs. 2 and 3. The upper pair of rolls is used for punching or sheeting the dough and the larger roll for the molding process. The large roll speed is 72 r.p.m. and the speed of the sheeting rolls is 164 r.p.m. The diameters of the sheeting rolls and molding drum are 1½ in. and 7 in., respectively.

Oven. A reel-type electric oven was designed and built to handle twelve micro bread pans. The micro oven is 18¼ in. wide, 21½ in. deep, and 34 in. high. The oven has provision for the use of steam. The door opening is 4-9/16 in. high and 8-7/16 in. long.

Loaf Volume Apparatus. The loaf volume apparatus is illustrated

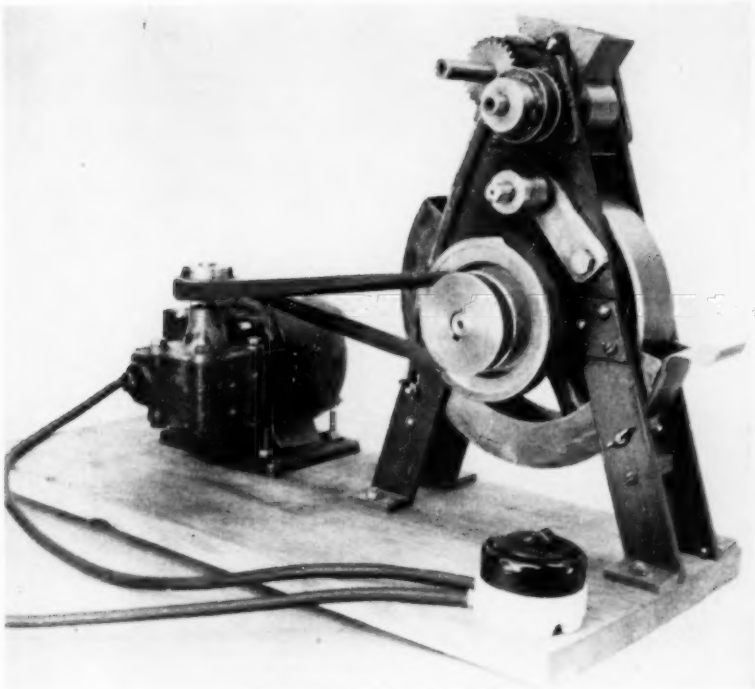


Fig. 2. Sheeting rolls and molder.

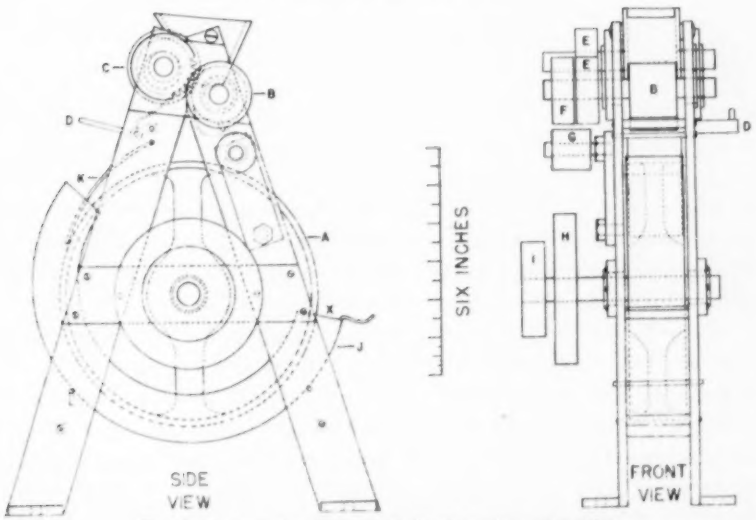


Fig. 3. Cross-section drawing of sheeting rolls and molder.

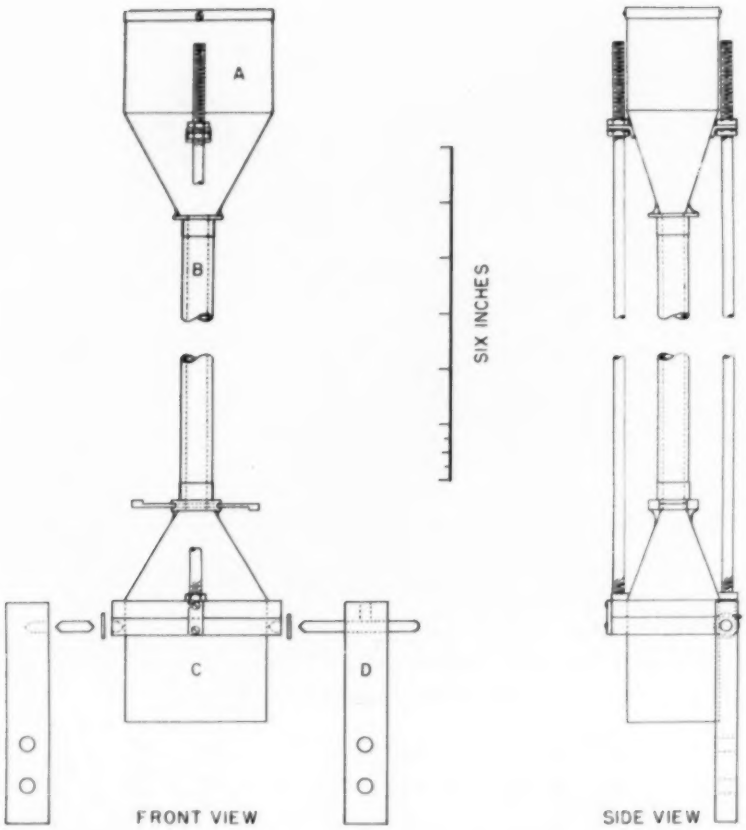


Fig. 4. Loaf volume apparatus.

in Fig. 4. It is of conventional hour-glass design but uses lead shot (about 441 shot per sq. in.) rather than seed for volume displacement. Rape seed was 'unsatisfactory owing to the static electrical charge produced by the seed rubbing against the glass (2).

Bread Pans. The bread pans were constructed of 16-gauge steel and have the following dimensions: 2.7 cm. wide and 4.2 cm. long at the bottom; 3.3 cm. wide and 5.0 cm. long at the top; and 2.3 cm. deep.

Micro Farinograph Bowl. A 10-g. mixing bowl for the farinograph is shown in Fig. 5. The special bowl[2] was used to determine flour

[2]The special micro bowl was designed and built in Germany and made available through the courtesy of C. W. Brabender and Pillsbury Mills Inc., Minneapolis, Minn. This equipment is not available commercially.

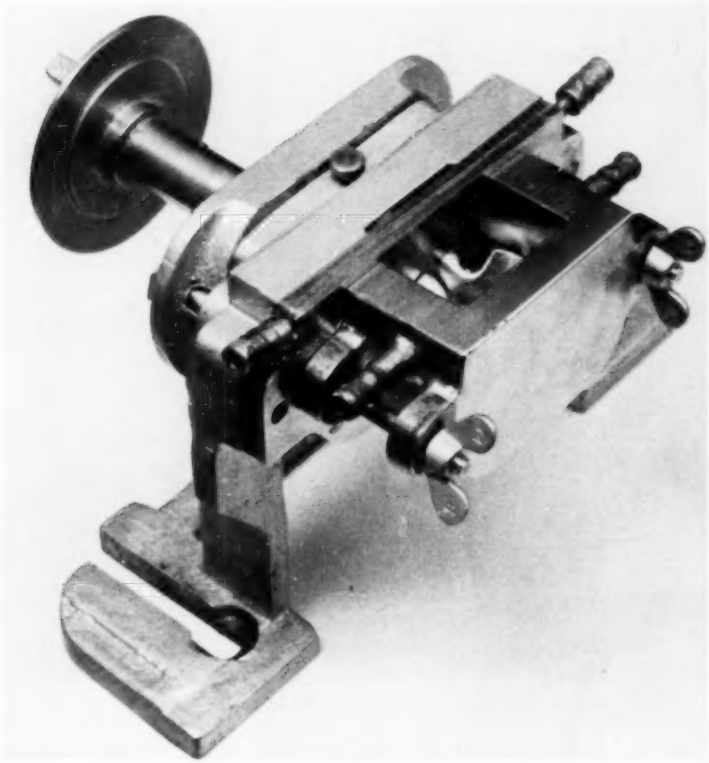


Fig. 5. Micro farinograph bowl.

absorption and the mixing characteristics of the dough. Use of the 10-g. bowl requires a special farinograph scale head with a range of 200 consistency units, a dynamometer bumper-arm, a special dampening piston, and a 10-ml. buret calibrated in units of 0.02 ml. (Fig. 6).

Micro Milling. The small samples of wheat were milled by the method described by Finney and Yamazaki (5). The validity of this method of milling has been shown by Finney *et al.* (3).

Results and Discussion

Using the micro equipment developed, comparisons were made between the standard A.A.C.C. baking test (1) and a micro baking method. The samples compared by the two baking procedures were the 1952 Kansas Experiment Station environment series (10) and a special group of wheat samples grown at Manhattan, Kansas, in 1952

Fig. 6. Farinograph with micro bowl and special scale head.

and tested by the Federal Hard Red Winter Wheat Laboratory, U.S. Department of Agriculture. Under the standard A.A.C.C. baking procedure, the loaf volumes ranged from 683 cc. to 1047 cc. with an average loaf volume of 852 cc. Under the micro procedure, loaf volumes ranged from 37 cc. to 62 cc. with an average loaf volume of 48 cc. The correlation between the two methods with different groups of samples ranged from $r = 0.749$ to 0.948.

Details of the baking procedure will be reported later. Mixing time, weight of dough, fermentation time, and oven time and temperatures are at present being modified as experience is gained with the micro technics. Several hundred wheat samples from several states are being processed in the laboratory. It is apparent that only slight modification of the standard A.A.C.C. formula or fermentation times is necessary for optimum baking conditions.

Comparisons were made of the farinograms obtained with the 10-, 50-, and 300-g. bowls using a baker's winter wheat flour, a baker's spring wheat flour, a family flour, and a pastry flour. The curves are

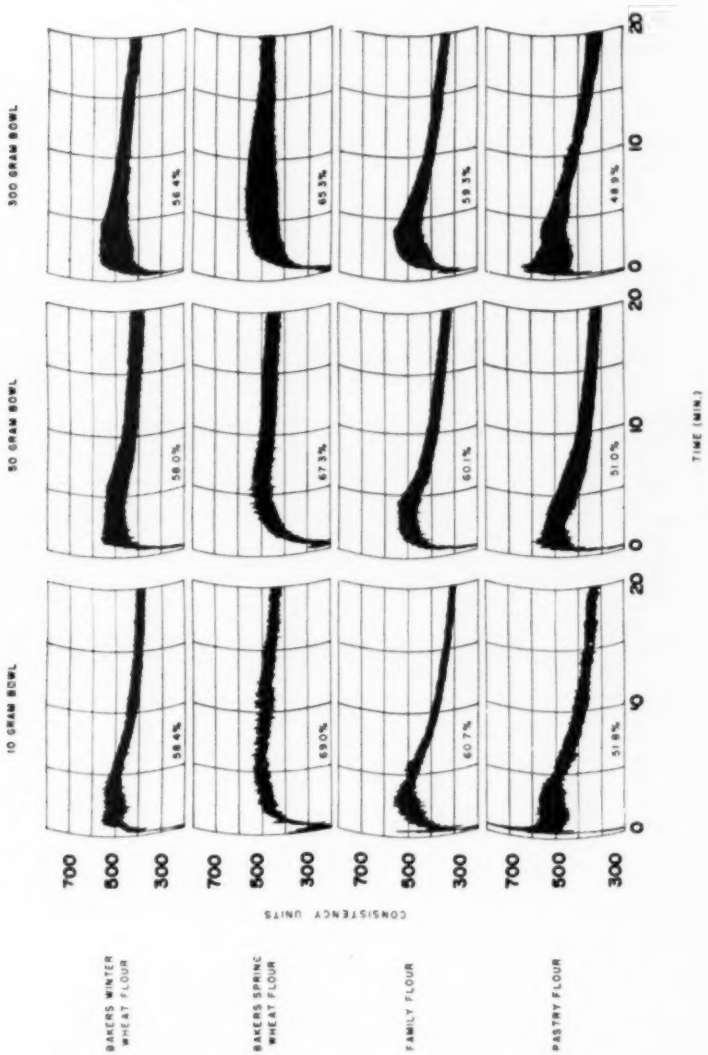


Fig. 7. Comparison of farinograms made with the 10-, 50-, and 300-g. farinograph bowls.

shown in Fig. 7: within each flour type there is good agreement. Some variation was experienced in measuring absorption, but in every case the change corresponded to the bowl size (i.e., as the bowl size decreased, the absorption increased).

The results of this investigation indicate that the same degree of mechanization is possible with the micro method as with the standard A.A.C.C. method. The testing by micro methods at an early generation of large numbers of samples from the wheat breeding programs will decrease the time and expense involved in the development of new wheats.

Literature Cited

1. American Association of Cereal Chemists. Cereal laboratory methods (5th ed.). The Association: St. Paul, Minnesota (1947).
2. Cathcart, W. H., and Cole, C. L. Wide-range volume-measuring apparatus for bread. Cereal Chem. **15:** 69–79 (1938).
3. Finney, K. F., Heizer, H. K., Shellenberger, J. A., Bode, C. E., and Yamazaki, W. T. Comparison of certain chemical, physical, and baking properties of commercial, Buhler, and Hobart-milled flours. Cereal Chem. **26:** 72–80 (1949).
4. Finney, K. F., Morris, V. H., and Yamazaki, W. T. Micro versus macro cookie baking procedures for evaluating the cookie quality of wheat varieties. Cereal Chem. **27:** 42–49 (1950).
5. Finney, K. F., and Yamazaki, W. T. A micro-milling technique using the Hobart grinder. Cereal Chem. **23:** 484–492 (1946).
6. Geddes, W. F., and Aitken, T. R. An experimental milling and baking technique requiring 100 grams wheat. Cereal Chem. **12:** 696–707 (1935).
7. Geddes, W. F., and Frisell, B. An experimental flour mill for 100-gram wheat samples. Cereal Chem. **12:** 691–695 (1935).
8. Harris, R. H., and Sanderson, T. A comparison between the 100 and 25 gram baking methods. Cereal Chem. **15:** 251–256 (1938).
9. Robinson, R. J., and Shellenberger, J. A. Microdetermination of protein in cereal products. Ind. Eng. Chem. (Anal. Ed.) **4:** 243–245 (1932).
10. Shellenberger, J. A., Johnson, J. A., Laude, H. H., Palmer, D. L., and Miller, G. D. Milling and baking characteristics of Kansas wheat varieties. Kansas Agr. Expt. Sta. Cir. 303, March (1954).
11. Van Scoyk, W. V. Micro-baking technique, applications and results. Cereal Chem. **16:** 1–12 (1939).
12. Werner, E. E. The baking test Cereal Chem. **2:** 310–314 (1925).

PROGRAM CONTROL ATTACHMENT FOR MIXERS ELIMINATING HUMAN ERRORS[1]

HELEN BAFDER, MARY KIMBALL, AND C. G. HARREL

ABSTRACT

An automatic cake mixing machine has been developed for use in the quality control of prepared cake mix production. This equipment is also suitable for checking other types of food products.

The timing apparatus, consisting of three cam-operated microswitches, controls the speed and time of mixing, as well as the volume and flow of liquid. The beaters perform the scraping down requirement.

This machine increases the uniformity of results, saves time, and eliminates human errors in the mixing operation.

The preparation of cake batters has always required extreme skill. Experience is needed to mix a batter precisely according to any given recipe and to obtain the same results with similar conditions. In quality control work with prepared cake mixes, uniformity of mixing becomes particularly important. To eliminate human errors which occur in the mixing procedures and in weighing or measuring the liquid, an automatic mixing and measuring device has been developed.

Control Attachments

The device consists of a synchronized timer-cam mechanism and liquid feed-in system adapted for use with a standard food mixer. A photograph of the mixer with the control attachments is shown in Fig. 1.

The modifications made on this mixer were as follows:

a. The wire slopes of the beaters were reshaped to scrape the bowl above the batter level and were covered with plastic hose to obtain perfect bowl scraper action. This eliminated the necessity for stopping the mixer to scrape the bowl during the operation and resulted in a uniformly mixed batter. Plastic hose was selected which did not absorb fat and was not abrasive in action.

b. A starter button was added on the side of the mixer so that the operator could start the mixing operation easily.

c. Electrical connections were made from the motor of the machine to the timing mechanism. The wires from the liquid feed-in device were connected directly to the cam mechanism.

d. To the mixer motor was added a speed control mechanism of

[1]Manuscript received June 10, 1954. Presented at the Annual Meeting, May, 1953. Contribution from Pillsbury Mills Research and Development Laboratories, Minneapolis, Minnesota.

Fig. 1. Automatic cake mixing machine with attachments.

conventional design for varying the speed of the mixer. A two-speed governor controlled by an electro-magnetic system changed the speed from high to low to comply with the specific speed needed for the cake recipe being used.

A diagram of the liquid dispensing mechanism is shown in Fig. 2. It is mounted on an upright support (A), anchored at its bottom to the mixer base. The cup (B) containing the liquid is slightly tapered at the bottom with an outlet (C) placed so as to discharge the liquid into the mixing bowl. The cup contains:

a. An overflow stand pipe or gauge tube (D) placed so that the opening is located at a predetermined distance above the bottom of the cup to limit the amount of liquid and permit only a predetermined volume to be discharged.

b. A needle valve (E) which opens and closes the liquid outlet.

c. A solenoid (F) that lifts the needle valve into an open position. The operation of this mechanism is based on volume delivery of liquid. The gauging tube is placed inside the cup so that when all the liquid is added, variation in the total amount of liquid is minimized. This gauging tube is easily replaced with other tubes for recipes requiring different total volumes of liquid.

The synchronized timing mechanism is shown in Fig. 3.

The timer consists of three cams, mounted one above the other as a connected unit. Each cam is made from a sheet metal plate with

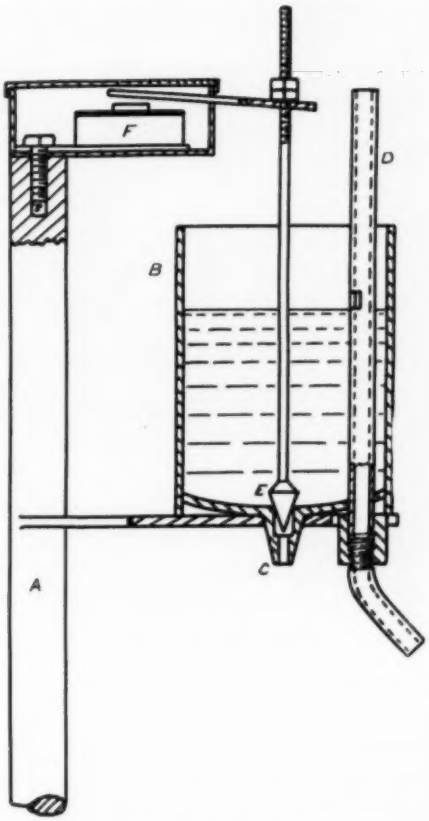


Fig. 2. Diagram of liquid dispensing device.

cut-out edges to control the micro-switches. The top cam controls the speed and length of mixing time. The middle cam controls the addition of liquid through the electro-magnetic mechanism which lifts the needle valve. The bottom cam controls the starting and stopping of the mixer motor. A screw cap clamps the cams tightly against the base of the timing device. Different sets of cams are used to produce the desired timing sequence needed for any food product which has a definite cycling or repeated action.

Operation of Mixer

A prepared mix or dry ingredients are put into the mixing bowl. The appropriate liquid is added to the cup of the liquid dispensing

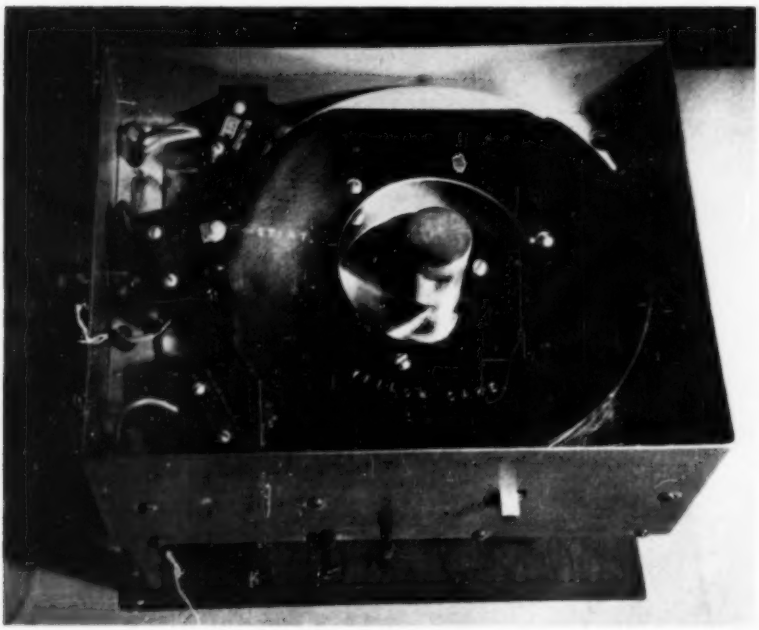


Fig. 3. Timer mechanism.

device. The motor of the mixer is started by pressing the button which starts the switches on the time cycling mechanism. Depending on the recipe, a certain volume of liquid is added in prescribed increments to the dry mix and a certain speed and length of mixing time is followed. After completion of the cycle for this product, the cake batter needs only to be put into pans by the operator and baked.

The timing cam mechanism has a specific starting position and is so labeled on the top cam. Once the machine is started, the cycling mechanism can be stopped in the middle of a cycle, if necessary, by pulling the electric switch and then started again only at the point where it stopped. It cannot be recycled, but must finish the cycle it is on.

The control attachments have been found to be very durable. The cam mechanism has a cover so that no mix can be dropped into it. With reasonable care the machine can be used extensively with little trouble. The spring governor in the rear of the motor may need to be adjusted from time to time to keep the speed regulated, and the mixer switches may need to be replaced once a year with constant use of the machine.

At present these control attachments cannot be applied to all types of mixers since the ability to overcome the scraping down requirements is a pre-requisite to the successful application of any automatic timing device.

Use of the automatic mixer under quality control conditions has proved highly satisfactory. Variations in liquid deliveries were reduced from about 6% to 2.5% by its use. To check this variation further, the weight of milk delivered was determined using the automatic dispensing device, a graduated cylinder, and an ordinary household measuring cup. Twenty-five deliveries by each of these methods were made for each of the two liquid additions required in a yellow cake mix recipe and the weights recorded. Volumes were calculated using the specific gravity of the milk as measured with a hydrometer. Standard deviations determined from these figures are presented in Table I.

TABLE I

STANDARD DEVIATIONS OF LIQUID ADDITIONS TO THE YELLOW CAKE MIX

	1st Addition		2nd Addition		Total	
	ml.	*% of mean*	*ml.*	*% of mean*	*ml.*	*% of mean*
Measuring cup	3.21	1.8	2.40	2.1	4.34	1.5
Graduated cylinder	0.50	0.3	0.53	0.5	0.76	0.3
Automatic dispenser	2.00	1.8	2.39	1.3	1.60	0.6

As expected, standard deviations obtained with the measuring cup were greatest although the individual deliveries from the automatic mixer showed variations nearly as large. Variability in total volume delivered, which is of greatest importance, was very low for both the automatic dispenser and the measurements made with the graduated cylinder.

The automatic dispenser has greater accuracy of delivery than either the graduated cylinder or the measuring cup. The total volume can be regulated by adjusting the overflow level so that the proper volume of liquid is delivered. In the measuring cup or graduated cylinder a portion of the liquid adheres to the walls of the vessel and the amount delivered is consequently not the amount measured. The discrepancy will vary with the amount of drainage permitted with each delivery. Adherence of liquid to the walls of the automatic dispensing unit is of no consequence after it has been properly set to deliver a specific amount of liquid. Thus the automatic dispensing unit is at least as dependable as careful successive measurements of liquid in a graduated cylinder and definitely superior to measurements made with a measuring cup.

Discussion

From the standpoint of uniformity of production with a minimum of technical skill, this cake timing mechanism is extremely valuable in the laboratory. It will control substantially the entire mixing operation and produce precisely the same mixing steps for any particular series of batters. Furthermore, one operator can use three of these machines as compared to one standard mixing machine. The advantages of the program control attachment for laboratory mixers include a saving of time, reduced operator fatigue, and the elimination of human errors.

Acknowledgments

The need for such equipment was clearly expressed by Emery Swanson and the equipment was developed by Mr. Carl W. Brabender of Pillsbury Mills, Inc. A patent has been applied for and it is expected that a competent manufacturer will be licensed so that the equipment will be available at a reasonable cost.

THE CARBOHYDRATES OF THE GRAMINEAE. III. A NOTE ON THE NATURE OF WHEAT GUM[1]

K. A. Gilles[2] and F. Smith[3]

During investigations into the structure of the water-soluble gums obtained from cereal grains (1), the presence in wheat starch of a polysaccharide containing pentose sugars was noted.

Thus when a commercial sample of wheat starch (25 g.) is extracted with water (500 ml.) at 70° C. for about 1 hour and the extract treated with three volumes of methanol, a polysaccharide is precipitated (yield 5% approx.). This substance appears to be a mixture of wheat gum and a polyglucosan (probably water-soluble starch), the latter arising from broken starch granules.

By the usual technics of paper chromatography (2, 3, 4, 5) this polysaccharide mixture, which gives a blue color with iodine, has been shown to contain glucose (63.2%), arabinose (5.3%), and xylose (3.2%).

Extraction of the more highly purified samples of wheat starch with water in the manner described above affords a glucosan (soluble

[1] Manuscript received July 2, 1954. Paper No. 3200, Scientific Journal Series, Minnesota Agricultural Experiment Station.
[2] General Mills Research Laboratory, Minneapolis, Minnesota.
[3] Department of Agricultural Biochemistry, University of Minnesota.

starch), but little or no pentose-containing polysaccharide.

A similar wheat gum containing pentose sugars is found in the sulfite wash-water from the commercial separation of starch from wheat flour. The polysaccharide, precipitated directly from the wash-water with alcohol, was an amorphous white powder which showed $[\alpha]_D^{25} -20°$ in *N* sodium hydroxide solution and contained glucose (58%), arabinose (17%), and xylose (25%).

It would appear that it is this pentosan-containing material (wheat gum) which has an adverse effect on the separation of both the starch and the gluten fractions of wheat flour (6). It is also apparent that the presence of wheat gum in starch wash-water not only presents a pollution problem but it also represents the loss of valuable material. Potentiometric determinations of amylose in wheat starch by iodine sorption methods might be subject to error on account of the presence of wheat gum.

The chemical constitution of wheat gum will form the subject of a later communication.

Acknowledgment

The authors thank Mr. G. V. Caesar of the Huron Milling Co., Harbor Beach, Michigan, for providing the samples of wheat starch and sulfite wash-water.

Literature Cited

1. Gilles, K. A., Meredith, W. O. S., and Smith, F. The carbohydrates of the *Gramineae*. The constitution of the water-soluble polysaccharides of the grain of barley *(Hordeum vulgare)*. Cereal Chem. **29:** 314–316 (1952).
2. Partridge, S. M. Filter-paper partition chromatography of sugars. I. General description and application to the qualitative analysis of sugars in apple juice, egg white, and foetal blood of sheep. Biochem. J. **42:** 238–248 (1948).
3. Hough, L., Jones, J. K. N., and Wadman, W. H. Quantitative analysis of mixtures of sugars by the method of partition chromatography. Part V. Improved methods for the separation and detection of the sugars and their methylated derivatives on the paper chromatogram. J. Chem. Soc. 1702–1706 (1950).
4. Partridge, S. M. Application of the paper partition chromatogram to the qualitative analysis of reducing sugars. Nature **158:** 270–271 (1946).
5. Dubois, M., Gilles, K., Hamilton, J. K., Rebers, P. A., and Smith, F. A colorimetric method for the determination of sugars. Nature **168:** 167 (1951).
6. Clendenning, K. A., and Wright, D. E. Separation of starch and gluten. V. Problems in wheat starch manufacture arising from flour pentosans. Can. J. Research **28F:** 390–400 (1950).

THE CARBOHYDRATES OF THE GRAMINEAE. IV. IDENTIFICATION OF THE SUGARS OF THE FLOUR OF WHEAT (TRITICUM VULGARE)[1,2,3]

R. Montgomery and F. Smith

ABSTRACT

The simple sugars and oligosaccharides have been extracted from wheat flour with aqeuous ethanol and separated by chromatography. The following sugars have been identified by the formation of crystalline compounds: glucose, fructose, sucrose, and maltose. The presence of glucofructosans of small molecular weight was also indicated by paper chromatography.

In a previous paper in this series (4), the quantitative chromatographic analysis of the sugars in a Southwestern baker's patent wheat flour was reported. Glucose (0.01%), fructose (0.02%), sucrose (0.10%), maltose (0.07%), and two other components believed to be melibiose (0.07%), raffinose (0.18%) and undetermined amounts of oligosaccharides containing levosine were present. These results were similar to those reported by Williams and Bevenue (10), who also used chromatographic techniques and who also calculated the amount of the slow moving levosines as 0.82%.

It was realized (4) that these results were tentative, being based solely upon chromatographic analysis, and that more definite evidence of the identity of the various sugars must await the characterization of the components by the isolation of crystalline compounds. Such a characterization of the sugars of an unbleached Southwestern baker's patent flour constitutes the subject of the work reported herein.

Materials and Methods

Extraction of Sugars. Eight hundred and thirty grams of an unbleached Southwestern baker's patent wheat flour (moisture, 13%; protein, 10.8%, expressed on a 14% moisture basis) were suspended in 1850 ml. of boiling 90% ethanol and heated at 80° for 1.5 hours to inactivate any enzymes. The mixture was centrifuged to give extract A and the insoluble residue extracted three times with 75% ethanol (1500 ml.) at reflux for 2 to 3 hours to give successively extracts B, C,

[1]Manuscript received August 5, 1954. Contribution from the Department of Agricultural Biochemistry, University of Minnesota, St. Paul 1. Paper No. 3202 of the Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2]This paper is a partial report of research done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Northern Utilization Research Branch of the Agricultural Research Service.

[3]Part I of this series was published in Cereal Chem. **28:** 424 (1951); Part II in J. Am. Chem. Soc. **76:** 5309- (1954); and Part III in Cereal Chem. **31:** 488-489 (1954).

and D. Each extract was kept at 5° for at least 24 hours during which time a yellow proteinaceous material precipitated, from which the mother liquors were separated by decantation. The yellow proteinaceous material was not investigated further. Two more samples of flour (820 g. and 800 g.) were extracted as before using the extracts A, B, C, and D in that order. The final extracts, from which a large amount of protein had been precipitated at 5°, were combined and evaporated under reduced pressure to remove the ethanol. The resulting aqueous suspension was maintained at 5° for several days and any further protein precipitate was separated by decantation of the supernatant liquid. The latter was concentrated to 300 ml. at 35–40° under reduced pressure, excessive foaming being partially controlled by the liberal addition of capryl alcohol. The concentrate, which was yellow and colloidal in nature, was stored at 5°.

Partial Separation of Sugars by Displacement Chromatography on Charcoal (8). Equal weights of charcoal (Darco G 60)[4] and Celite 535[5] were mixed without previous sieving. A sample (40 g.) of this mixture was packed dry into a chromatographic tube to give a column of adsorbent, 160 mm. × 35 mm. To this column was added an aliquot (15 ml.) of the above concentrate of the sugars extracted from flour and development was made by the successive addition of water (1000 ml.), 5% (1000 ml.) and 15% ethanol (1000 ml.). The change of developing solvent was made when the eluate had become optically inactive for the last 250 to 500 ml. The material remaining on the column was extracted batchwise with 40% acetic acid or alternatively with boiling 30% ethanol and then 10% aqueous phenol at room temperature, which removed all the carbohydrate material from the column.

Each of the above fractions was evaporated to dryness at 35°–40° and the residue extracted with 2 to 5 ml. of water. To the aqueous solutions was added ethanol (3 volumes) and after centrifugation the supernatant liquors were evaporated to dryness. Each fraction afforded a mixture of sugars which was analyzed by paper chromatography using butanol[6]-ethanol-water as the irrigating solvent in the usual way (1, 3, 4).

Identification of Sugars. In general, the mixture of sugars in each fraction obtained from the carbon column was separated by chromatography on Whatman No. 3 paper using butanol: ethanol: water (4:1:5). By using a 22″ x 18″ sheet, it was possible to load each chro-

[4]Darco Corp., New York, N. Y. Mention of products or companies is not to be construed as an endorsement of these products or firms.
[5]Johns-Manville Co., New York, N. Y.
[6]Throughout this paper, "butanol" refers to the normal isomer, 1-butanol.

matogram with 100–250 mg. of sugar mixture (11). In the developed chromatogram, the sugar bands were located by cutting ¼" vertical strips from four positions on the dried sheet and spraying them with ammoniacal silver nitrate in the usual way. The individual bands were cut out and eluted with 50% ethanol. The corresponding bands from ten such chromatograms were combined and rechromatographed to give chromatographically pure sugars.

Results and Discussion

The sugars contained in the 70% ethanol extract of wheat flour when subjected to fractionation using a carbon-celite column (8) gave the results summarized in Table I.

TABLE I

CHARCOAL FRACTIONATION OF SUGARS EXTRACTED FROM WHEAT FLOUR BY 75% ETHANOL

Fraction Eluted by:	Weight	R_g[a] Value of Carbohydrate Components Located on the Chromatogram							
		1	2	3	4	5	6	7	8
	g.								
Water	0.32					0.39[b]		1.00	1.24
5% Ethanol	0.24		0.15		0.31[b]	0.43	0.65		
15% Ethanol	0.72	0.04	0.16		0.34	0.44[b]			
40% Acetic acid	0.25[c]	0.03		0.27		0.42	0.61	1.00	1.25

[a] R_g represents the mobility of the compound in question with respect to that of glucose.
[b] The spots were very faint.
[c] This fraction contained protein.

The fractionation into mono-, di-, tri-, and oligosaccharides was not complete (cf 8, Table I). However, the procedure did remove residual water-soluble protein from the first three fractions. By comparison with standard sugars, component 5 corresponded to maltose, component 6 to sucrose, component 7 to glucose, and component 8 to fructose. Components 2 and 4 had R_f values similar to those of raffinose and melibiose respectively.

It will be seen that elution with 40% acetic acid resulted in some hydrolysis of the higher molecular weight sugars since glucose and fructose were present in this fraction. Such hydrolysis is slight when the final extractions are made with 30% ethanol and then 10% aqueous phenol. The total recovery of sugars represented 1.4% of the wheat flour on a dry basis, which is in fair agreement with the results of other workers (4, 10) considering that different flours were used. Final fractionation into the pure sugars, by the use of Whatman No. 3 filter paper sheets (11), resulted in the identification of fructose, glucose, sucrose, and maltose as described below:

(a) *Fructose*, R_g 1.24 on butanol-ethanol-water, was converted to D-glucosazone, m.p. 207–208° and mixed m.p. with an authentic sample 205–206°.

(b) *Glucose*, R_g 1.00 on butanol-ethanol-water, acetylated with sodium acetate-acetic anhydride to give β-glucopyranose pentaacetate m.p. 131–132°, mixed m.p. with authentic sample 132–133°. Glucosazone was also formed in the usual way, m.p. and mixed m.p. 204–205°.

(c) *Sucrose*, R_g 0.66 on butanol-ethanol-water, was obtained partially crystalline and a few crystals were isolated m.p. 171–172°, mixed m.p. with sucrose, 180–181°. The mother liquor from the above crystallization was hydrolyzed with 0.01 *N* hydrochloric acid at 80° for 20 minutes. The hydrolysate was shown by paper chromatography with butanol-ethanol-water to contain only glucose, R_g 1.00, and fructose, R_g 1.23, and formed only glucosazone m.p. and mixed m.p. 204–205° when reacted with phenylhydrazine hydrochloride and sodium acetate in the usual way.

(d) *Maltose*, R_g 0.43 on butanol-ethanol-water, formed maltosazone, m.p. and mixed m.p. 204–205°.

(e) *Unknown I*, R_g 0.34 using butanol-ethanol-water, produced on hydrolysis fructose and glucose. No melibiose was detected in the hydrolysate.

(f) *Unknown II*, R_g 0.16 butanol-ethanol-water, produced on hydrolysis fructose, glucose and melibiose, R_g 0.40.

(g) *Unknown III*, a very small amount of material with a mobility on a paper chromatogram between that of raffinose and melibiose was obtained together with glucofructosans with mobilities less than raffinose.

Previous workers have identified glucose (5), sucrose (6) and raffinose (2, 7) in wheat flour or wheat germ by isolation of the crystalline sugars or their derivatives. The sugar component which behaved chromatographically like raffinose gave glucose, fructose, and melibiose upon mild acid hydrolysis. The amount of melibiose produced indicated that this component was a mixture of a glucofructosan and raffinose. The sugar which behaved like melibiose when chromatographed on paper using butanol-ethanol-water as the irrigating solvent, was found to give only glucose and fructose upon acid hydrolysis. This sugar component was, therefore, not melibiose since the latter gives galactose and glucose upon hydrolysis and like those oligosaccharides showing lower chromatographic mobilities with butanol-ethanol-water as the irrigating solvent, it is a member of a series of glucofructosans which differ from each other only in their fructose content (9, 10).

The results reported herein confirm the tentative chromatographic identification of glucose, fructose, sucrose, and maltose and in so doing verify the quantitative analytical figures reported in Part I of this series (4). However, the amount of raffinose reported can only be approximate as it was not completely separated from a glucofructosan before quantitative analysis. Moreover, the component tentatively reported as melibiose (4) was found to be a glucofructosan and again its concentration in wheat flour as reported earlier can only be approximate.

Literature Cited

1. Boggs, L., Cuendet, L. S., Ehrenthal, I., Koch, R., and Smith, F. Separation and identification of sugars using paper chromatography. Nature **166:** 520–521 (1950).
2. Dubois, M. Water soluble carbohydrates of the wheat germ. M. S. thesis, University of Minnesota, 1951.
3. Flood, A. E., Hirst, E. L., and Jones, J. K. N. Quantitative analysis of mixtures of sugars by the method of partition chromatography. Part I, Standardisation of procedure. J. Chem. Soc. 1679–1683 (1948).
4. Koch, R. B., Geddes, W. F., and Smith, F. The carbohydrates of *Gramineae*. I. The sugars of the flour of wheat *(Triticum vulgare)*. Cereal Chem. **28:** 424–430 (1951).
5. Liebig, H. J. von. Über den Zuckergehalt der feinen Weizenmehle, der Weizenmehlteige und der Vergorenen Mehlteige, sowie über die diastatische Kraft der Weizenmehle. Landw. Jahr. **38:** 251–271 (1909).
6. Schulze, E. Über die chemische Zusammensetzung der Samen unserer Kulturpflanzen. Landw. Vers. Sta. **73:** 35–170 (1910).
7. Schulze, E., and Frankfurt, B. Über das Vorkommen von Raffinose in Keim des Weizenkorns. Ber. **27:** 64–65 (1894).
8. Whistler, R. L., and Durso, D. F. Chromatographic separation of sugars on charcoal. J. Am. Chem. Soc. **72:** 677–679 (1950).
9. White, L. M., and Secor, Geraldine E. Occurrence of two similar homologous series of oligosaccharides in wheat flour and wheat. Arch. Biochem. Biophys. **43:** 60–66 (1953).
10. Williams, K. T., and Bevenue, A. The chromatographic examination of sugars in wheat flour. Cereal Chem. **28:** 416–423 (1951).
11. Zamecnik, P. C., Loftfield, R. B., Stephenson, Mary L., and Steele, Jean M. Studies on the carbohydrate and protein metabolism of the rat hepatoma. Cancer Research **11:** 592–602 (1951).

THE BREAD STALING PROBLEM. MOLECULAR ORGANIZATION OF STARCH UPON AGING OF CONCENTRATED STARCH GELS AT VARIOUS MOISTURE LEVELS[1]

N. N. Hellman,[2] Barbara Fairchild,[2] and F. R. Senti[2]

ABSTRACT

Starch gels containing 29% to 63% water were prepared by heating starch of the desired water content for 30 minutes at 95°C. Starch systems containing more than 43% water lost all crystallinity demonstrable by X-ray diffraction as a result of the heat treatment. Storage of the gels under conditions which prevented moisture loss permitted the starch to reorder and exhibit crystalline X-ray diffraction patterns. The moisture content at which the starch gels were aged determined the structural modification which appeared. Gels containing less than 29% water gave type A diffraction patterns; between 32% and 39% water content, the gels developed mixed A and B diffraction patterns which also might be classified as C diffraction patterns. Above 43% water content, the gels developed typical B diffraction patterns. Rate of crystallinity development at different moisture contents differed; however, in all cases it was essentially completed in 8 days. Gels containing 56% or more water showed low rates of crystallization and decreased amounts of molecular organization. Reheating of aged samples caused loss primarily of B-type crystallinity of the crystallization process. The type V diffraction pattern, described by Katz to be produced by freshly pasted starch gels, was shown to arise from a complex of starch with the fat normally present in wheat starch preparations.

The purpose of this report is to describe changes in the molecular organization of starch which occur in starch gels prepared and aged at moisture contents comparable to that of bread. In the pioneering investigations of J. R. Katz (3), it was shown by X-ray diffraction patterns that staling bread developed crystallinity and, moreover, that the crystalline regions responsible for the diffraction pattern occurred entirely in the starch component of bread. He applied the term "retrogradation" to the return of crystallinity in the starch of staling bread, using a word which had been applied earlier to the spontaneous development of insoluble starch in homogeneous aqueous solutions. During and following the baking process, the starch in bread undergoes transitions between several structural modifications. The diffraction patterns of these different structural modifications have been designated by Katz as "A," "B," and "V." The crystalline organization

[1] Manuscript received June 23, 1954. This paper reports research undertaken in cooperation with the Quartermaster Food and Container Institute for the Armed Forces, and has been assigned No. 491 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Department of Defense. Presented at the 39th annual meeting of the American Association of Cereal Chemists, held at Denver, Colorado, May 23-27, 1954.

[2] Northern Utilization Research Branch, Peoria, Illinois, one of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.

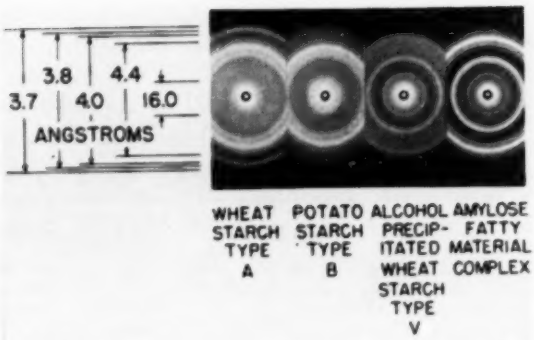


Fig. 1. X-ray diffraction patterns of starches and starch complexes.

which exists naturally in wheat starch of flour or dough produces the A diffraction pattern (Fig. 1). Katz reported that in the baking of bread the A pattern disappears inasmuch as the starch becomes largely amorphous. There were, however, a few weak lines on the diffraction pattern of fresh bread which Katz identified as the V pattern (Fig. 1). Katz held that starch with a similar V pattern could be prepared by alcohol precipitation of dilute starch gels or paste. As staling occurred, still another crystalline form appeared which was identified by its production of a B diffraction pattern (Fig. 1). This form occurred naturally in potato and other tuber starches. Katz observed that the intensity of the B diffraction pattern increased with time of staling. The development of the B pattern intensity was paralleled by decreases in soluble starch and swelling power and increases in crumbliness of the bread—all of these phenomena being characteristic of staling. Measures which inhibited staling also inhibited the development of crystallinity of the starch component.

Since the cessation of work by Katz on the X-ray diffraction patterns of bread there has been little work in this field. Hopper (1), investigating the effect of monoglycerides on bread staling, showed that the retardation of compressibility changes caused by these agents qualitatively corresponded to the retardation in the rate of starch crystallization. A major difficulty exists, however, in studies of the role of starch in bread staling when they are conducted on bread. Bread composition is so complex that to ascribe changes in bread specifically to changes in starch requires a better understanding of the behavior of starch in isolated systems as well as the behavior of other pure bread components. The work of Katz on starch, although extensive, carries few X-ray studies of starch at moisture contents comparable to that of bread. We present here a detailed X-ray study of the changes occur-

ring upon aging wheat starch gels in which the water content is limited to the range of interest in bread technology.

Experimental Methods

All starch was from a single batch processed, using laboratory procedures (4), from a sample of the 1950 crop of Thatcher wheat. Samples for X-ray study were adjusted to the desired moisture content by the following process. The sample (about 0.7 g. dry starch) was placed in a shallow layer in thin aluminum dishes (official moisture dishes of the American Oil Chemists' Society), covered with an excess of water, and then the excess water evaporated off in a desiccator containing a dish of saturated potassium nitrate solution producing 93% relative humidity. When the desired moisture content was reached, the dishes were covered, sealed with a layer of cellophane electrician's tape, and heated 30 minutes in a 95° C. oven. This gelatinization treatment was selected to simulate baking. From the initial weight of the dish, starch, and moisture, and the final weight after heating, the moisture content of the starch could be calculated before and after the heat treatment. In the work reported, the loss was restricted to less than 10% of the dry starch weight.

For X-ray examination, a 2-mm. diameter disk was punched from the starch layer in the dish and mounted in a hole in a 1-mm. thick cellulose acetate holder. This sample holder was sealed by interference-color-thin glass windows which were cemented on the sample holder with unpolymerized Thiokol rubber cement. This sample holder was mounted with wax on the back pinhole of the X-ray collimator. Nickel-filtered copper radiation was passed through the sample and the diffraction patterns were recorded on flat films at 5-cm. film-to-sample distance.

In each aging study, the closed aluminum sample container was stored at room temperature (estimated 24°±3° C.) in a small desiccator containing a dish of water. Sample disks were punched from the starch as needed, and a continuous check on the water content was made by weighing. At the termination of the experiment, the moisture content of the sample was determined by vacuum-oven drying. The moisture content of the terminal sample determined in this manner usually differed slightly from the moisture content calculated from the running weight during the course of the experiment. This difference probably resulted from the inability to make proper allowance for water loss on opening the tin for new samplings. The water content at which these samples are entered in the tables represents the water content of the sample at the initiation of storage. The final

water content was sometimes as much as 6% less. Moisture contents were determined by vacuum-oven drying at 105° C. and are expressed on a total basis, equivalent to g. of water per 100 g. of moist material.

It was highly desirable to measure quantitatively in the fresh and aged gels the relative amounts of amorphous material and the material which had crystallized to give A and B diffraction patterns. A rough estimate of crystallinity development evidenced in the X-ray films was made by use of comparison standards.

In order to simulate the diffraction patterns given by bread or by the concentrated starch gels, three series of comparison standards were prepared by exposing single films in sequence to several components. The components were 1) fresh amorphous gel which was in each case prepared immediately before making the X-ray diffraction pattern, 2) a 3-weeks-old gel aged at 29% water content which gave an A pattern, and 3) a 3-weeks-old gel aged at 50% water content which gave a B pattern. Each film in any of the comparison standard series was exposed for 3 hours, but the proportion of the exposure time contributed by any single component was systematically varied. Thus, each pattern simulated a mixture in which for each component the percentage of exposure time was considered equivalent to percentage composition. In the first series of comparison standards, the films were exposed to diffraction from the fresh amorphous gel and the gel giving an A pattern; in the second series, the film was exposed by using fresh amorphous gel and the gel giving a B pattern; and, in the third series, the film was exposed by using fresh amorphous gel, the gel giving an A pattern, and the gel giving a B pattern. The patterns in the first series thus formed a scale for judging those gels which aged to give A patterns; the patterns in the second series served for the gels which aged to give B patterns; and the patterns of the third series were used for judging mixed A and B patterns. By comparing the X-ray patterns of the gels at different ages with these known combinations, we obtained a semiquantitative measure of the rates of crystallization.

The term "crystallinity" is used to describe the presence of molecular organization sufficient to give a discrete line on the X-ray diffraction pattern. The measurements of crystallinity reported are not on an absolute scale. Thus, the maximum crystallinity development in our patterns is given a scale value of 100 but may be caused by only one-fifth or one-tenth of the starch in the sample being crystalline.

Results

The characteristic X-ray diffraction patterns of starches are shown

in Fig. 1. These patterns were obtained by X-ray exposure of samples in air-dry condition. The A pattern, characteristic of cereal starches (Fig. 1), is distinguished by the diffuse unresolved doublet at 3.8 A; and the B pattern, characteristic of tuber starches, by the 16 A central spacing and the sharply defined rings at 3.7 and 4.0 A. A third pattern, C, which is characteristic of tapioca starch, exhibits a 16 A central spacing of variable intensity and a diffuse band at 3.8 A of variable intensity. In this study, however, instead of labeling a pattern as C, we shall assign proportions of A and B patterns for the purpose of better describing the variable intensities of the 16 A and 3.8 A lines.

One other type of X-ray diffraction pattern is involved in these studies—that given by the amylose complex with fatty material (Fig. 1). It was thought that in the gelatinization process the amylose component of starch would combine with fat which is present naturally in the wheat starch granule and give rise to amylose-fat complex. This material is identified by a strong 4.4 A line in the freshly heated gel (Fig. 2). Katz identified this diffraction pattern, calling it the V pat-

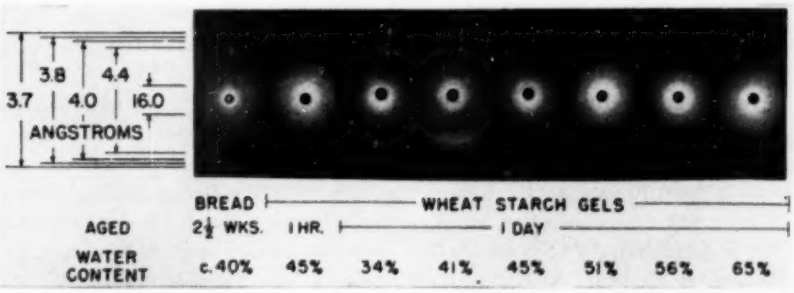


Fig. 2. X-ray diffraction patterns of staled bread and wheat starch gels prepared and aged at various water contents.

tern, as the same pattern produced by freshly alcohol-precipitated starch. Such alcohol-precipitated starch, exhibiting the V diffraction pattern, is extremely labile in the presence of sufficient water, and we should anticipate its conversion if it were present in bread to another structure which would give the B pattern. However, the V pattern from freshly baked bread persists through staling.

Both the V pattern from freshly alcohol-precipitated starch and the pattern of the amylose-natural fat complex contain an intense line near 4.4 A. The amylose-alcohol and amylose-fat complex differ in structure, however, although they have been shown to possess a structural similarity inasmuch as they are based on a helical configuration of the starch polymer chains (5,6).

Experimental proof that the 4.4 A line in freshly heated starch gels arose primarily from the amylose-fat complex was obtained by examining the X-ray pattern of a defatted wheat starch gel. A sample of wheat starch was extracted three times for 48 hours each, with 85% methanol in a Goldfisch extraction apparatus, to remove fatty materials. The starch was then washed thoroughly with water and dried. A sample was heated at 95° C. for 30 minutes with 43.5% water. The X-ray pattern of the gel showed practically complete removal of the line normally present at 4.4 A.

A summary of the crystallization changes observed on gelatinizing and aging wheat starch is given in Table I. It was observed that at a moisture content below 29% the pattern of freshly heated sample differed only slightly from the A pattern of the original unheated moist starch. Heating at water contents increasingly greater than 29% resulted in the fresh gel exhibiting increasingly greater destruction of the crystallinity giving an A pattern and appearance of fat-amylose complex pattern. Heating at 43% or greater water content resulted in only the 4.4 A line of the fat-amylose complex appearing in the fresh gel (Fig. 2). At water contents above 43%, the intensity of the fat-amylose complex pattern was reduced, probably as a result of sample dilution.

After aging for 1 day the gels containing 29% to 35% water showed an A pattern, but the diffuse halo at 16 A was progressively stronger and sharper as the moisture content increased. At 37% water, there was a definite line at 16 A, and the line at 3.8 A began to broaden. This generally is classified as a C pattern but, for the reasons stated in the Experimental Methods Section, we chose to consider this a mixed A and B pattern. At 43% water content, the 1-day-old gel gave a definite B pattern with sharp 16 A line and doublet at 3.7 and 4.0 A. The most intense B pattern at the 1-day age was found in the region of 47% to 50% water content. Greater water contents in the gel resulted in progressive loss of the intensity but no loss in sharpness of the B pattern. The above-described changes in the diffraction patterns are illustrated in Fig. 2.

Samples aged 8 days with moisture contents below 35% exhibited only A patterns. In the range of 35% to 43%, the samples after 8 days of aging showed progressively more intense B patterns the higher the water content. Although, as previously noted, 1-day-old gel at 43% water content gave a sharp B pattern, on aging the X-ray pattern showed in addition characteristics of the A pattern. All samples at 47% water content and above yielded solely the B pattern. Starch gels containing more than 50% water crystallized more slowly, and to

TABLE I

SURVEY OF CRYSTALLIZATION CHANGES ENCOUNTERED ON HEATING AND AGING WHEAT STARCH GELS AT VARIOUS MOISTURE CONTENTS

Moisture Content	X-ray Diffraction Pattern of Paste		
	Freshly Pasted[a]	1 Day Old	8 Days Old
%			
29	Practically no intensity decrease of A pattern	Equivalent to original unheated starch suspension	Slightly stronger A pattern than original suspension
32	Progressive decrease in A pattern intensity and increase in fat complex pattern intensity	Dominantly A pattern, but progressive strengthening of 16 A diffuse halo characteristic of B patterns	
35	Same as above	Same as above	A pattern dominant with approximately 10% B
37	Same as above	Dominant A, but definite 15 A line and broadening of 3.8 A line signalling appearance of B pattern	A pattern dominant with approximately 25% B
39	Equivalence of strength of A and fat complex patterns	Progressive development of mixed A and B pattern with doublet of 3.8 A unresolved	A pattern dominant with approximately 35% B
43	Only fat complex pattern remains	Definite, well-developed B pattern with doublet at 3.7 and 4.0 A	Resolved doublet at 3.7 and 4.0 A merges into diffuse ring

(*Continued on next page*)

TABLE I (Continued)

Moisture Content	X-ray Diffraction Pattern of Paste		
	Freshly Pasted[a]	1 Day Old	8 Days Old
%			
46	Progressive decrease of fat complex pattern intensity as a result of dilution	Only B pattern develops	Typical B pattern
50		Region of maximum B pattern intensity	Region of maximum B pattern intensity
56		Onset of weakening of B pattern intensity	
59			Onset of weakening of B pattern intensity
63		Very weak B pattern intensity, 10% of intensity of pattern obtained with 50% moisture	Weak B pattern intensity, 20% of intensity obtained at 50% moisture

[a] Samples were treated by heating in sealed containers 30 minutes at 93° C.

a lesser extent the higher the water content. Crystallization was so inhibited in the gel having 63% water content that it gave a B pattern only one-fifth as strong after 8 days of aging as found in the samples aged at 50% water content.

The pattern from staled bread (Fig. 2), baked at 60% absorption and 2½ weeks old, is comparable to that of a starch gel aged at approximately 40% water content.

The change in pattern with aging, as measured semiquantitatively by comparison with reference patterns, is given in Fig. 3. These data

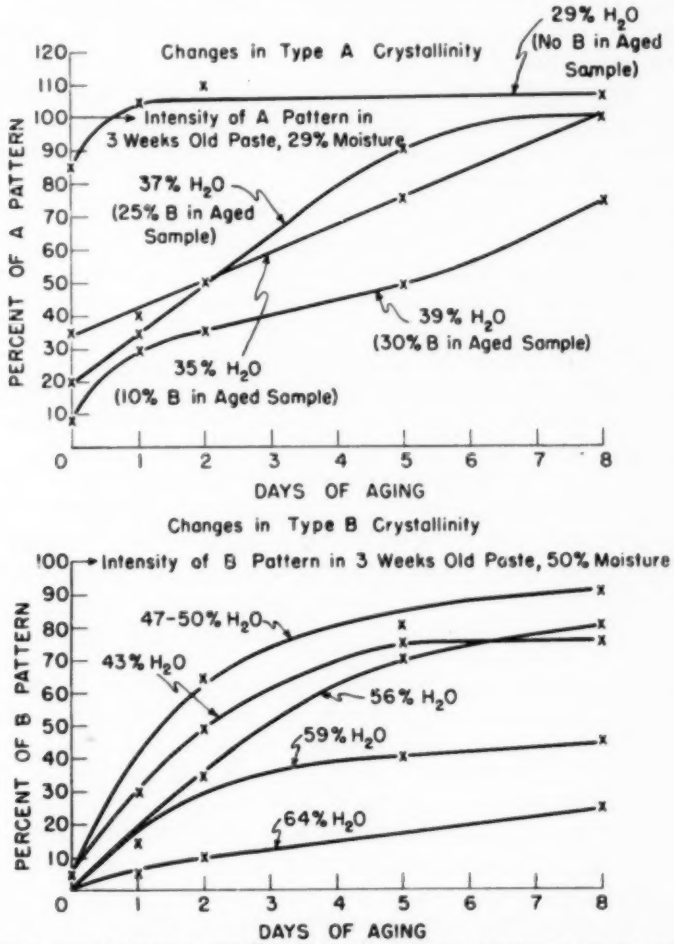

Changes in Type A Crystallinity
29% H2O
(No B in Aged Sample)
Intensity of A Pattern in 3 Weeks Old Paste, 29% Moisture
37% H2O
(25% B in Aged Sample)
39% H2O
(30% B in Aged Sample)
35% H2O
(10% B in Aged Sample)
PERCENT OF A PATTERN
DAYS OF AGING
Changes in Type B Crystallinity
Intensity of B Pattern in 3 Weeks Old Paste, 50% Moisture
47-50% H2O
43% H2O
56% H2O
59% H2O
64% H2O
PERCENT OF B PATTERN
DAYS OF AGING

Fig. 3. Rate of change in crystallinity of starch pastes as a function of time and moisture content.

show the extent of crystallization found in a given sample as a percentage of that in the reference sample which developed only the A pattern (3 weeks old, 29% moisture preparation) or the reference sample which developed only the B pattern (3 weeks old, 50% moisture preparation). It should be noted that the pattern from samples aged at 35%, 37%, and 39% water content are treated as if they are mixtures of A and B patterns, although it may be more correct to describe them as mixtures of A or B patterns with a C pattern. Also, the ordinate in this figure is not to be construed as the absolute extent of crystallization because in the reference sample only about 15% of the starch is sufficiently uniformly organized to contribute to the line pattern. From these data it might appear that crystallization processes leading to pure A or B patterns are more rapid than the process leading to mixed A and B or C patterns; however, this must be more thoroughly substantiated by obtaining better data with a more precise procedure for intensity measurement.

Reheating of aged samples causes changes in the X-ray pattern, indicating reversal of the crystallization process only for the B-type crystallinity. Thus, reheating an 8-days-old gel containing 32% water for 30 minutes at 70°C. caused very little change in its A pattern, nor did any change in the resulting X-ray diffraction pattern occur on aging the sample. Reheating samples containing 39% and 40% water removed much of the B but very little of the A pattern. On aging the reheated samples, the A pattern remained more prominent than in the original aged sample. Reheating an aged sample with a well-developed B pattern and a water content of approximately 45% caused partial loss of crystallinity which returned at a rate equivalent to that found during the original aging of the sample. These above data are only preliminary and the effect of reheating should be subjected to a systematic investigation.

Discussion

These data have shown that the changes in molecular organization occurring on aging wheat starch gels are critically dependent on the moisture content of the starch gel. There is a critical moisture content which is necessary before a given heat treatment will cause loss of original starch granule crystallinity; there are critical moisture contents which determine whether an A, B, or mixed A and B diffraction pattern develops on aging of gels. These critical moisture contents all lie in the range of moisture contents encountered in bread technology.

The crystallization results show a striking parallel to the swelling power behavior of aged starch pastes reported by Katz (2). The effect

of aging on the swelling power did not appear until starch was gelatinized with 30 g water/100 g dry starch. The most marked change in swelling power appeared at 55 g water/100 g dry starch, and above 200 g. water the changes again become minimal. In the present study, loss of the A pattern did not appear until the starch was heated with 32 g water/100 g dry starch; above about 125 g water/100 g dry starch, the return of crystallization was much retarded. At 200 g water/100 g dry starch, the return of crystallinity was extremely slow.

Although these results demonstrate the dependence of changes in aged starch pastes upon the moisture content of starch, the importance of particular types of crystallinity to the bread staling problem is yet to be assayed. It may be presumed that an intimate relation exists between these crystallization processes and the firming of bread. Although many of these starch phenomena parallel in a rough fashion the course of bread staling, there has not yet been established a good quantitative relation between the extent of these processes and the subjective evaluation of staling. The complexity of the changes demonstrated, however, show the need for caution in extrapolating measurements of starch-water systems at high water content to the staling bread system.

Literature Cited

1. Hopper, R. P. Information concerning the making of quality bread from the standpoint of softness, tenderness, and keeping quality – an evaluation of monoglyceride shortenings in bread. Proc. Am. Soc. Bakery Eng. **25:** 63–70 (1949).
2. Katz, J. R. Gelatinization and retrogradation of starch in relation to the problem of bread staling. *In* A comprehensive survey of starch chemistry, Vol. 1, pp. 100–117; R. P. Walton, ed. Chemical Catalog Company: New York (1928).
3. Katz, J. R. X-ray investigation of gelatinization and retrogradation of starch in its importance for bread research. Bakers' Weekly **81:** 34–37, 46 (March 24, 1934).
4. MacMasters, M. M., and Hilbert, G. E. The composition of the "amylodextrin" fraction of wheat flour. Cereal Chem. **21:** 548–555 (1944).
5. Mikus, F. F., Hixon, R. M., and Rundle, R. E. The complexes of fatty acids with amylose. J. Am. Chem. Soc. **68:** 1115–1123 (1946).
6. Rundle, R. E., and Edwards, F. C. The configuration of starch in the starch-iodine complex. IV. An X-ray diffraction investigation of butanol-precipitated amylose. J. Am. Chem. Soc. **65:** 2200–2203 (1943).

A METHOD FOR THE RAPID DETERMINATION OF MOISTURE IN DOUGHS AND BREADS[1]

HOWARD W. LINCOLN, B. M. DIRKS AND C. G. HARREL[2]

ABSTRACT

The moisture content (total volatile matter) of dough and bread may be determined in 10 minutes or less by means of a projection reading balance and two infrared lamps. The sample is pressed between two tared filter papers which are then separated and placed back to back for drying on a balance arm between the two lamps. The method gave results in good agreement with moisture data obtained by the regular air oven or vacuum oven procedures. The standard error of a single determination was 0.45% moisture for doughs and 0.09% moisture for bread.

Definitions and Standards of Identity for Bakery Products under the Federal Food, Drug, and Cosmetic Act(s) require that bread, rolls, and buns contain not less than 62% of total solids (5). The official method (2) for carrying out this determination requires that the sample be air-dried for approximately 16 hours, ground, and the residual moisture determined by drying either for one hour in an air oven at 130°C. or for 5 hours in a vacuum oven at 100°C. with not more than 25 mm. mercury pressure. This method is not practical for routine control since most commercial baked products are delivered before such a determination could be completed. A method for the rapid determination of moisture in baked products would be of considerable value. Since the quality and uniformity of baked products and efficient bakery operation depend greatly upon the amount of water used in preparing doughs, it would also be advantageous to know the total solids content at various stages in the baking procedure.

A procedure for the quick determination of total solids would thus be valuable for the following:

1. Providing a check on the water content of the dough as it comes from the mixer. The amount of water added at the mixer could be calculated from known moisture contents and percentages of other ingredients.
2. Determining the gain or loss in percent of total solids as a result of fermentation, evaporation or absorption.
3. Predicting the moisture content of bread from the moisture content of the dough before baking.
4. Checking the total solids content of baked bread before it leaves the bakeshop.

[1] Manuscript received July 26, 1934. Presented at the Annual Meeting, May, 1934.
[2] Research and Development Laboratories, Pillsbury Mills, Inc., Minneapolis, Minnesota.

Since there is no quick and satisfactory method for the determination of total solids in doughs and bread, the procedures to be described in this paper have been found useful. The method involved pressing the dough or bread sample between tared filter papers followed by rapid drying of the pressed sample between two infrared lamps while suspended from one arm of a projection reading balance.

Materials and Methods

The equipment employed in these experiments is shown in Fig. 1.

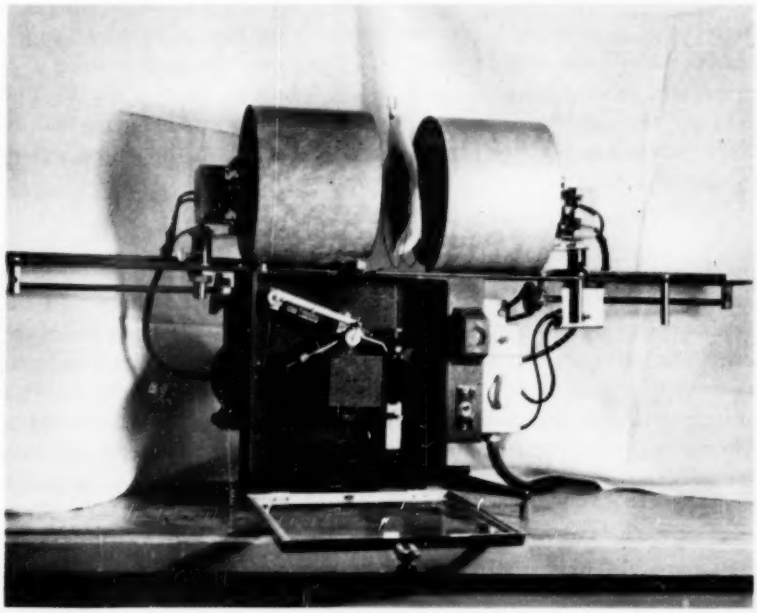


Fig. 1. Apparatus for rapid determination of moisture in dough or bread. The dough on the filter papers in the machine contains a red dye.

A projection reading balance was provided with facilities for suspending the sample from one balance arm between two 1550 watt infrared lamps. The lamps were connected to a 220 volt current supply through a 5-position selector switch which permitted the use of 0, 425, 650, 950, or 1600 watts in each lamp. The lamps were mounted on $\frac{3}{8}$" lead screws having 16 threads per inch and a reversible electric motor moved the lamps in or out at 0.8 cm./min. by revolving the screws at 5 r.p.m. This feature was added during the investigation to minimize charring of bread samples and still give results in the shortest

possible time which were in good agreement with those obtained by usual methods. Adjustable stops permitted starting and stopping the lamps at any predetermined point.

The sample was pressed between tared Whatman No. 4, 18.5 cm., filter papers with a Carver Laboratory Press at 12,250 p.s.i. Five grams of dough formed a thin disc approximately 12 cm. in diameter and 0.2 mm. thick. A 10 g. bread sample pressed into a disc approximately 11 cm. in diameter and 0.6 mm. thick. No detectable non-volatile solids were forced through the filter paper by the treatment. Only traces of color appeared on the back side of the filter paper when water-soluble or fat-soluble dyes were used in making up doughs for pressing and there was no increase in dry weight of a second set of filter papers placed outside the original ones. After pressing, the papers were separated and placed back to back before clipping in the tester. This exposed the sample and decreased the drying time. Taring of the filter papers was accomplished by clipping them in the tester, drying to constant weight (1 min.) and balancing.

Application of the Procedure to Doughs

Moisture (total volatile matter) determinations were made on flour-water doughs, yeast-leavened bread doughs, chemically-leavened biscuit doughs, and commercially available refrigerated biscuit doughs. With the exception of the refrigerated doughs, determinations were made immediately after mixing. The tester lamps were held in a stationary position 7.6 cm. from the sample and were set at 950 watts. The drying time for a 5 g. sample was 3.5 minutes. Prolonged drying beyond 3.5 minutes under these conditions did not bring appreciable changes in the indicated moisture. The total time required for a single determination was 5 to 6 minutes.

The results were compared with those obtained by drying 2 g. samples for 5 hours at 100°C. in a vacuum oven under a pressure of 25 mm. mercury. The data for flour-water doughs were also compared with values calculated from the moisture content of the flour and the amount of water used.

Typical results obtained with the various types of doughs employed are presented in Table I. The infrared procedure gave moisture results which compared very favorably with calculated values and those obtained by the vacuum oven method. The largest absolute discrepancy observed in this set of determinations was 1.0% which was only 2% of the total moisture. The standard error of a single determination based on the variation between replicate determinations for the various groups of samples listed in Table I was 0.45% moisture which

TABLE I

MOISTURE DETERMINATIONS ON VARIOUS TYPES OF DOUGHS

Dough Type	Moisture Content, %						Deviations of Infrared Tester Values as Percent Moisture		
	Infrared Tester				Vac. Oven	Calculated	Vac. Oven	Calculated	Standard Error[a]
	1	2	3	Mean					
Flour-Water	46.4	46.0	46.0	46.1	46.1	46.3	0.0	−0.2	
	47.4	47.2	47.0	47.2	47.7	48.0	−0.5	−0.8	
	48.2	49.6	49.6	49.1	49.4	49.5	−0.3	−0.4	0.50
					Av. Deviation		−0.3	−0.5	
Yeast-Leavened	43.6	44.8	45.0	44.5	45.5		−1.0		
	45.8	45.6	46.6	46.0	47.0		−1.0		0.65
					Av. Deviation		−1.0		
Chemically-Leavened	34.4	33.6	33.6	33.9	34.2		−0.3		
	37.6	37.3	37.2	37.4	37.2		0.2		
	39.1	38.8	39.2	39.0	38.7		0.3		0.32
					Av. Deviation		0.1		
Refrigerated Biscuit	38.4	38.4	38.5	38.4	37.8		0.6		
	38.2	38.6	38.8	38.5	38.5		0.0		
	38.4	37.6	38.0	38.0	37.6		0.4		
	38.2	37.6	38.6	38.1	37.9		0.2		
	37.0	37.0	37.8	37.3	37.5		−0.2		0.38
					Av. Deviation		0.2		
	ALL SAMPLES						−0.1		0.45

[a] Single determination.

compares well with a standard error of 0.31% moisture obtained for vacuum oven moistures on a similar series of doughs.

From the standard errors given for each individual dough, the greatest variations occurred with the yeast-leavened bread dough. In addition, the infrared results for this dough had the largest average deviation from the vacuum oven results. The higher values obtained in the vacuum oven were probably due to fermentation and the consequent production of volatile materials which occurred before the dough reached a temperature sufficiently high to kill the yeast. Anderson (1) has reported that 90 to 100 minutes are required to raise the sample temperature to an oven temperature of 100°C. when a dried sample of flour was used. Since the specific heat of cereal products increases with increasing moisture (4), a longer time would be required for dough temperatures to reach the oven temperature. This would allow time for considerable yeast action before being inactivated. In the tester, the sample would reach an inactivating temperature almost immediately and this source of error would be minimized.

Application of the Procedure to Bread

The moisture content of bread varies from one portion of a loaf to

another and, in order to apply the infrared method to the determination of moisture in bread, it was necessary to obtain a sample representative of the entire loaf.

Sampling Procedure. To secure a representative bread sample with negligible loss of moisture and solids, an entire loaf was ground in a Readco sausage grinder. This was used in conjunction with a Type D4-80 Readco mixer having a 2 h.p. motor. One revolving knife blade revolved inside a face plate containing 66-3/16 in. holes at a speed of 90 r.p.m.

The loaves were weighed and ground immediately. The ground material was caught in tared polyethylene bags and reweighed. Forty-two 1 lb. loaves were ground by this method. The loss in weight averaged 0.36 g. with a maximum loss of 1.0 g. Assuming the losses to be entirely moisture, they would only amount to 0.08% and 0.22% of moisture, respectively, on loaves containing 38% moisture.

To test for the uniformity of sampling, 12 loaves of commercial bread were ground as described. The ground material was transferred to fruit jars which were sealed and thoroughly shaken. Moisture de-

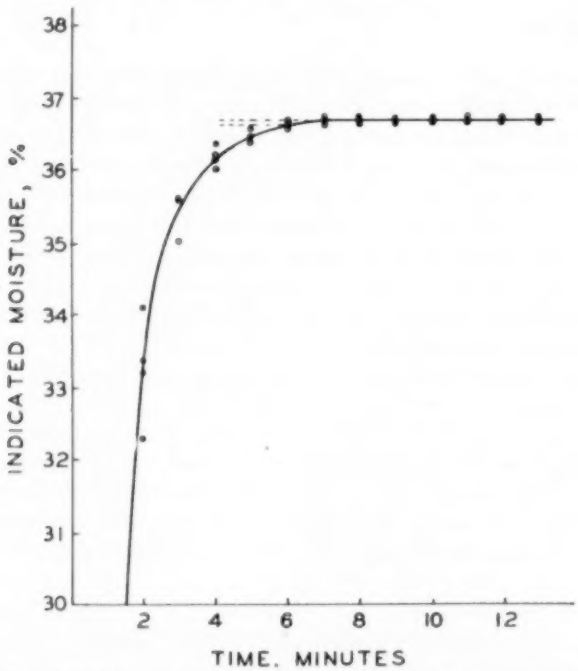


Fig. 2. Change of indicated bread moisture with time in the infrared moisture tester.

terminations were conducted on triplicate 10 g. samples from each loaf by drying at 130°C. for three hours. In addition, a total of 40 determinations were conducted on the ground material from one of these loaves using the same drying procedure. Standard error calculated from the triplicate determinations on each of the 12 loaves was 0.28% moisture. Calculated from 40 determinations on one loaf, the standard error was 0.23% moisture.

These figures indicate good uniformity in the ground material. A further check of uniformity was made visually by observing the results of grinding a composite loaf made of alternate slices from two loaves of bread, one of which contained a water-soluble red dye. The ground material was very uniform in color.

Determination of Bread Moistures by the Infrared Procedure. Ten gram portions of the ground bread were pressed between filter papers in the same manner as the 5 g. of dough. Several rates of drying with and without retracting the lamps were tried. The best procedure was found to consist of applying 950 watts with the bulbs retracting during the entire test period from a point 4.5 cm. from the sample. As soon as 30% moisture had been removed the bulbs were switched to 650 watts for the remainder of the determination. As illustrated in Fig. 2, 8 minutes were required to reach a constant value. There was little charring of the sample and results were in good agreement with those obtained by usual methods.

To compare the results for the infrared procedure with those obtained by the usual two-stage drying methods, loaves were divided in half by alternate slices. One half was ground as described above and the other half air-dried and then ground preparatory to the final dry-

TABLE II

COMPARISON OF MOISTURE DETERMINATIONS ON BREAD

Sample	Moisture Content, %							Deviations of Infrared Tester Values as Percent Moisture	
	Infrared Tester					Air Drying Followed by		Air Oven	Vac. Oven
	1	2	3	4	Av.	Air Oven	Vac. Oven		
1	35.9	36.0	36.0	36.0	36.0	36.1	36.0	−0.1	0.0
2	34.9	35.1	35.2	35.2	35.1	34.9	34.9	0.2	0.2
3	36.6	36.7	36.7	36.6	36.7	36.6	36.6	0.1	0.1
4	35.8	36.0	35.8	35.9	35.9	36.1	36.0	−0.2	−0.1
5	36.6	36.8	36.6	36.6	36.7	36.6	36.6	0.1	0.1
6	35.9	36.1	36.1	36.1	36.1	36.0	35.9	0.1	0.2
7	36.6	36.8	36.7	36.7	36.7	36.8	36.7	−0.1	0.0
8	36.7	36.8	36.7	36.9	36.8	36.8	36.8	0.0	0.0
9	35.9	35.8	35.8	35.8	35.8	35.7	35.7	0.1	0.1
						Average Deviation		0.0	0.1
	Standard Error				0.09				

ing step in the air or vacuum oven. This procedure was presumed satisfactory to give two samples with the same moisture content since Bailey (3) has shown that half loaves of bread (diagonally opposite quarters) provide representative samples for the determination of moisture.

Table II presents results obtained on nine loaves of commercial white bread. Deviations of results by the infrared procedure from those obtained with the vacuum oven method ranged from 0.2% (Sample No. 2) to −0.1% (Sample No. 4) moisture. When compared with the air oven method the deviations were 0.2% and −0.2% for the same samples. Standard error based on the replicate determinations for each loaf was only 0.09% moisture which was somewhat better than that obtained by drying ground samples 3 hours in an oven at 130°C. Duplicate 2-stage moisture determinations on each of 6 loaves of bread gave a standard error of 0.18%.

Discussion

The infrared procedure for determining the total solids content of dough and bread samples pressed between filter papers gave results which were in satisfactory agreement with the usual air-oven and vacuum-oven methods. The determination can be carried out in 10 minutes or less and it therefore provides a practical means for quality control. This apparatus need not be limited, however, to control of moisture in bread and doughs. Favorable preliminary data indicate that it may be useful in determining the moisture content of freshly tempered wheat. This has been a problem of long standing. It should have further value in any instance where a lengthy drying procedure would result in decomposition or production of volatile materials which may result in misleading moisture values.

Acknowledgments

The authors wish to give full credit to C. W. Brabender for the original idea and design of the equipment. (A patent has been applied for by C. W. Brabender and assigned to Pillsbury Mills, Incorporated, and it is Pillsbury's desire to make this equipment available to the industries interested as soon as a competent manufacturer has been found.)

The technical assistance of Betty Brooking is also acknowledged.

Literature Cited

1. Anderson, J. E. Some facts concerning vacuum-oven moisture determinations. Cereal Chem. 13: 437–452 (1936).
2. Association of Official Agricultural Chemists. Official methods of analysis (7th Ed.). Assoc. Offic. Agr. Chemists: Washington, D. C. (1950) p. 209.

3. Bailey, L. H. Report on sampling and determination of moisture in bread. J. Assoc. Official Agr. Chem. 14: 488–489 (1931).
4. Disney, R. W. The specific heat of some cereal grains. Cereal Chem. 31: 229–239 (1954).
5. Food and Drug Administration, Service and Regulatory Announcements — Food, Drug, and Cosmetic: No. 2, Part 17 (1952).

RAPID DETECTION OF MERCURY ON CEREAL GRAINS[1]

D. K. Cunningham and J. A. Anderson

ABSTRACT

Rapid detection of normal amounts of common mercury-containing fungicides in small samples of wheat, barley, rye, or oats has been facilitated by modification of Lepper's method.

In the revised method, fifteen treated seeds are boiled in alkaline reducing solution with 4 sq. mm. of 1/32-in. aluminum foil. The presence of mercury is indicated by the appearance of the aluminum surface and by bubbling after application of sodium alizarin sulfonate reagent.

Fungicides containing mercury have become increasingly popular for treating seed grain. Since mercury is poisonous, the Board of Grain Commissioners for Canada prohibits persons from offering grain treated with mercurial or other poisonous compounds for storage or sale at country elevators. Administration of this regulation requires a test for mercury contamination in grain samples.

A simple and rapid qualitative test devised by Lepper (4), depending on the formation of a hydroxide when aluminum is exposed to mercury in alkaline solution, has been used in modified form in this laboratory for some fifteen years (2, p.46). The quantitative method developed by Klein (3) has also been tried; it is sensitive but rather time-consuming. We have recently found that with aluminum foil instead of aluminum wire the Lepper test gives more clear-cut results and may be applied to barley, rye, or oats as well as to wheat. Furthermore, by suitably adjusting the quantities of reagent, and by employing Feigl's (1) sodium alizarin sulfonate reagent, the test for mercury can be carried out on fifteen treated kernels. The following sections describe the modified method in its final form and the experiments which led to its development.

[1] Manuscript received July 12, 1954. Paper No. 135 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg, Manitoba, and No. 316 of the Associate Committee on Grain Research.

Method

Fifteen kernels are placed in a test tube (10 mm. × 55 mm.) and 1 ml. of reagent is added. This consists of equal parts of 5% potassium hydroxide and 25% sodium thiosulfate, made up separately and mixed together as required. The mixture is brought to the boil on a sandbath and a piece of aluminum foil 2 mm. square and 1/32 in. thick is dropped in. Boiling is continued for 1 minute. The aluminum is then removed, rinsed with water, dried with acetone, and examined. A positive reaction is shown by the presence of small pits on the surface of the aluminum slips or by white alumina crystals. Figure 1, A shows a test piece on which only pits are evident, and Fig. 1, B shows

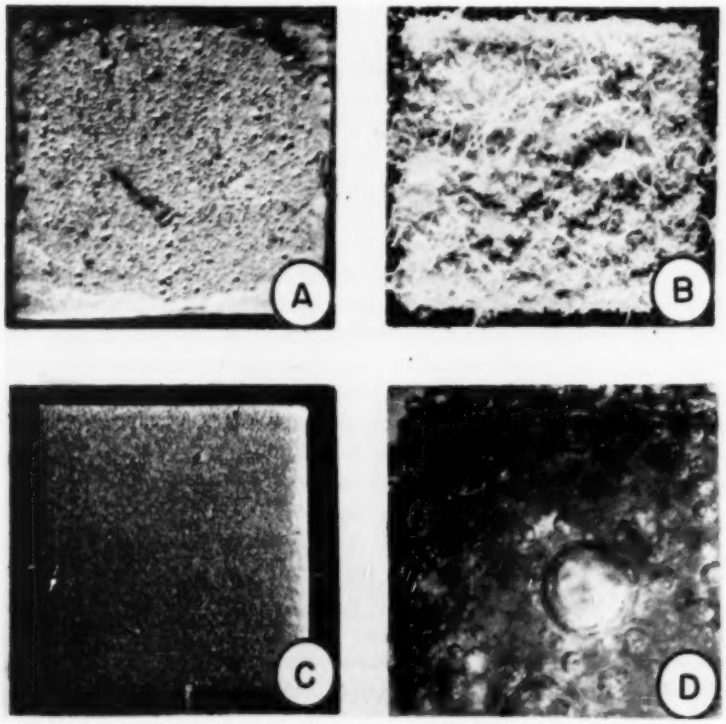


Fig. 1. Test pieces showing (A) pitted surface; (B) alumina crystals; (C) blank test; (D) sodium alizarin sulfonate-acetic acid test.

development of alumina crystals. A control test, in which the aluminum was boiled with the reagent only, is shown in Fig. 1, C. For these illustrations slightly larger pieces of foil, 9 sq. mm., were used to facilitate reproduction.

Further confirmation of the presence of mercury can be obtained by immersing the dried test piece in a drop of 1% sodium alizarin sulfonate in 10% acetic acid. Alumina resulting from the amalgamation of aluminum and mercury forms a brick-red stain with sodium alizarin sulfonate, and bubbles of gas (Fig. 1, D) are formed by action of the acetic acid on amalgamated aluminum so that a red froth results. This confirmatory test gives clear-cut results even with test pieces on which only pits have developed.

Experimental

Preliminary tests were made with a sample of aluminum wire of unknown origin available in the laboratory. This wire yielded positive results for wheat and rye, but failed for barley and oats. A new sample of pure aluminum wire gave anomalous results for wheat and oats. Finally a sample of pure aluminum foil (1/32 in. thick) was obtained from the Fisher Scientific Company. This foil gave clear differentiation between treated and untreated kernels for each cereal.

The optimum size of foil was determined by boiling pieces of aluminum foil 4, 8, 16, and 64 sq. mm. in area with 3 μg. of mercury as mercuric acetate in 0.5 ml. of reagent solution. The test showed that the smallest piece of aluminum gave the most positive reaction; still smaller pieces tended to dissolve completely in the boiling solution. A standard size of 2 mm. square (4 sq. mm.) was selected for the remaining studies.

The reaction was practically instantaneous for mercuric acetate solution. For commercial mercurial fungicides at least 1 minute of boiling was required. Further boiling did not make the test more positive. A reaction time of 1 minute was therefore fixed for the standard method.

The material used to develop the test consisted of average samples of No. 2 Manitoba Northern Wheat, No. 2 Canada Western Six-row Barley, No. 2 Canada Western Rye, and Extra No. 3 Canada Western Oats. Each of these lots was divided into three portions; one was treated with Ceresan M (ethyl mercury p-toluene sulfonanilide) at the rate of 0.5 oz. per bu.; another was treated with liquid Panogen (methyl mercury dicyan-diamide) at the rate of 0.75 oz. per bu.; the remainders were kept for blank control tests. After the test had been developed using these treated samples, kernels treated with nineteen other commercial fungicides containing mercury were also tested. All responded to the test in about the same degree as Panogen or Ceresan.

Under practical conditions, it may happen that treated grain is mixed with untreated grain. With fungicides such as Panogen, con-

taining a dye which stains the kernels and fluoresces under ultraviolet light, treated kernels can be readily segregated: this is more difficult with Ceresan and other dusts. Experiments have shown that fifteen treated kernels invariably give a positive test, and positive results are sometimes obtained with as few as five kernels.

If admixtures of kernels treated with Ceresan or other mercurial dusts are suspected, segregation of individually treated kernels may not be possible. Under these conditions the macro method (2) may be used with 10 g. of grain, 10 ml. of reagent, and 9 sq. mm. of foil in place of wire. The foil is boiled with the reagent for 3 minutes and then examined as in the micro test. The macro test is capable of detecting 1 g. of wheat treated with a normal dose of Ceresan or other mercurial dusts in 9 g. of untreated wheat; this is equivalent to a mercury concentration of about 2 p.p.m. Should the macro test prove inadequate the much longer method of Klein (3) may be resorted to, by which concentrations of mercury of 0.5 p.p.m., or even less, can be estimated by digesting larger samples of wheat.

Literature Cited

1. Feigl, F. Qualitative analysis by spot tests, inorganic and organic applications (3rd ed.). pp. 53–54. Elsevier Publishing Co.: New York (1946).
2. Grain Research Laboratory, Board of Grain Commissioners for Canada. Fourteenth Annual Report (1940).
3. Klein, A. K. Report on mercury. J. Assoc. Offic. Agr. Chemists **35:** 537–542 (1952).
4. Leppik, W. A test for mercury in treated seeds. Landw. Vers. St. **117:** 1–2, 109–112 (1933).

APPLICATION OF AMPEROMETRIC TITRATION TO THE DETERMINATION OF POTASSIUM BROMATE IN FLOUR[1]

D. K. Cunningham and J. A. Anderson

ABSTRACT

Armstrong's (1) modification of the Howe method (4) for determination of potassium bromate in flour has been further modified by use of a simplified amperometric technique (6) for determination of the iodine end point. When dilution caused by moisture in the flour is taken into account in calculating results, recoveries of bromate average about 97.5%. Standard errors of about ±0.15 p.p.m. are obtained with flour containing 5 to 15 p.p.m. of bromate, whereas the error is about ±0.37 p.p.m. at levels of 30 to 40 p.p.m.

Rainey (7) has recently published a comprehensive review of methods for determining potassium bromate in flour. The latest and perhaps the most promising of these methods are the titrimetric procedures of Howe (4) and Armstrong's modification (1). They differ mainly in that Howe titrates directly with thiosulfate the iodine released by oxidation of iodide with extracted bromate, whereas Armstrong uses excess thiosulfate and back titrates with idodate. Both methods have large errors at low concentrations of bromate, presumably because of the difficulty of the end point (7). In this laboratory low-grade flours have given additional trouble because the color of the extracts masks the end point.

It appeared that advantage might be gained by using the amperometric titration, for detection of the iodine end point, developed by Knowles and Lowden (6). In this simplified procedure the usual rotating platinum electrode is replaced by a stationary electrode of platinum foil, 2 sq. cm. in area, and the reference electrode is a saturated calomel one of the type made for pH meters. While the amperometric determination of the end point takes a little longer, and may thus be objectionable for routine assays, it provides a more objective and precise procedure which has advantages for reference and research purposes.

A description of the method, and of results obtained with it in determining bromate in flour, is given in the following sections.

Method

The method is based on the extraction and reaction procedures of

[1] Manuscript received July 29, 1954. Paper No. 136 of the Grain Research Laboratory, Board of Grain Commissioners for Canada, Winnipeg, Manitoba, and No. 317 of the Associate Committee on Grain Research.

Armstrong (1) combined with the amperometric titration of Knowles and Lowden (6).

Apparatus. (1) Glassware, comprising 500-ml. Erlenmeyer flasks, 250-ml. centrifuge tubes, 50-ml. beakers, and a 5-ml. micro-buret graduated in 0.01 ml. (2) Sargent Ampot or similar equipment with platinum electrode (2 sq. cm. in area) and calomel reference electrode.

Reagents. (1) Zinc sulfate, 103.4 g. per liter. (2) Sodium hydroxide, 26.0 g. per liter. (3) Sodium thiosulfate, 0.001 *N*. (4) Potassium iodate, 0.001 *N*. (5) Potassium iodide, 30%. (6) Sulfuric acid, 10%.

Method. Weigh 40 g. of flour into a 500-ml. Erlenmeyer flask and add 200 ml. of distilled water. Break up lumps by swirling and shaking, or with a glass rod if necessary, and allow to stand for 5 minutes. Add 25 ml. of zinc sulfate solution and 25 ml. of sodium hydroxide solution, and allow to stand 5 minutes. Centrifuge in 250-ml. bottles at *ca.* 1500 r.p.m. for 10 minutes.

Pipet into a 50-ml. beaker 25 ml. of the supernatant extract, 5 ml.

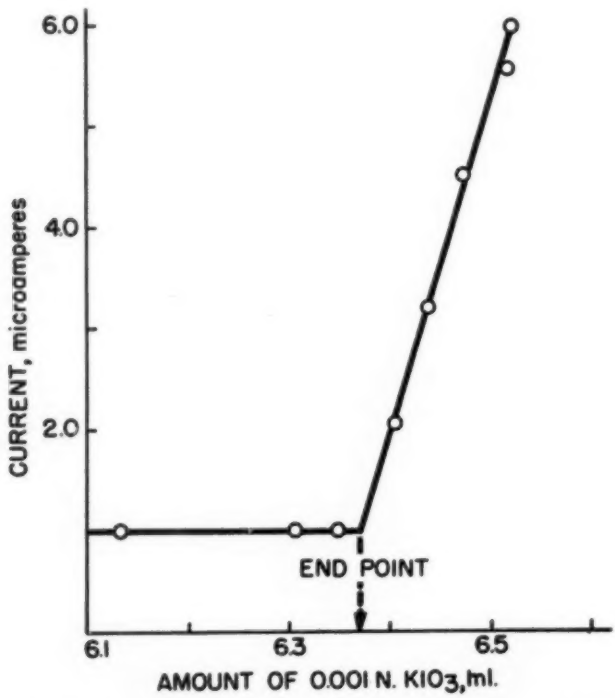


Fig. 1. Curves illustrating graphical determination of the end point.

of 0.001 *N* sodium thiosulfate solution, 5 ml. of 10% sulfuric acid, and 3 ml. of 30% potassium iodide solution. Titrate immediately with 0.001 *N* potassium iodate solution. A reagent blank must be run daily on 5 ml. of 0.001 *N* sodium thiosulfate.

The end point for the titration is determined graphically; typical results are shown in Fig. 1. As the current remains constant during the titration, two or three readings establish the initial line parallel with the x axis. At the end point a rapid linear increase in current begins and three or four readings establish the second line. When the two lines have been plotted, their intersection determines the end point. About 5 minutes are required for the titration and plotting.

Bromate concentration on an as-is basis in p.p.m. is calculated as follows:

Potassium bromate, p.p.m. =

$$(\text{Blank} - \text{titration}) \times (\text{N of iodate}) \times \frac{1}{25}\left[250 + \frac{40 \times \%\ \text{moisture}}{100}\right] \times \frac{167.01}{6} \times \frac{1000}{40}$$

This equation reduces to the following form:

$$(\text{Blank} - \text{titration}) \times (\text{N of iodate}) \times \left[2500 + (4 \times \%\ \text{moisture})\right] \times 2.78$$

Experimental

A comparison was first made of the accuracy of the titration for bromate in aqueous solution and in flour extracts. Duplicate determinations were made at concentrations equivalent to 2.5, 5, 7.5, 7.5, 10, 12.5, 15, 20, 25, 30, 35, and 40 p.p.m. in flour. Average recoveries (required, 17.5 p.p.m.) and standard errors were: $99.8 \pm 0.58\%$ (17.46 ± 0.14 p.p.m.) for aqueous solutions, and $97.7 \pm 0.96\%$ (17.11 ± 0.16 p.p.m.) for bromate added to flour extracts.

Possible interference by flour constituents was examined by extracting 10, 20, 30, and 40 g. of flour with 192 ml. of water and adding 8 ml. of solution containing 400 μg. of potassium bromate. After 5 minutes, the extracts were clarified and bromate was determined. Recoveries were 99.0, 97.5, 98.5, and 99.2%, and it thus appears that interference from flour constituents is negligible.

Recovery of bromate added to flour in dry form was also checked. A concentrated premix of 0.050 g. of potassium bromate in 250 g. of corn starch was ground in a ball mill for 3 hours. Portions of the premix were then added to untreated flour to give bromate levels of 5, 10, 20, and 40 p.p.m. Duplicate samples, with duplicate titrations

for each, gave the following recoveries: 102, 103, 98, and 98.5%.

Armstrong (1) noted that ammonium persulfate should not interfere with the determination as its rate of reaction with potassium iodide in dilute solutions is very slow. This was confirmed in experiments with 2,000 p.p.m. of ammonium persulfate and bromate levels of 10, 20, 30, and 40 p.p.m. which gave an average recovery of 99.6%. Among other common flour improvers iodate interferes in the sense that it is determined as bromate.

Hoffer and Alcock (3) noted a greater apparent loss of bromate with their colorimetric method when lower-grade flours were analyzed. Low-grade flours had also given trouble in this laboratory with the Armstrong method because they yield dark extracts. Accordingly, it seemed advisable to compare the recovery of bromate from flours of different grades.

Four commercial flours, first patent, bakers' grade, first clear, and second clear, were treated with potassium bromate at levels of from 5 to 40 p.p.m., in steps of 2.5 p.p.m., by slurrying 40 g. of flour with water, adding the required amount of bromate and diluting to 200 ml. Average recoveries (required, 22.5 p.p.m.) of bromate and standard errors were as follows:

	First Patent	*Bakers Grade*	*First Clear*	*Second Clear*
Recovery, p.p.m.	20.50	20.42	20.87	20.38
Standard error, p.p.m.	0.27	0.28	0.21	0.38
Recovery, %	97.7	97.4	99.5	97.2
Standard error, %	1.8	1.1	1.5	2.0

While average recoveries were lower than those obtained in some other experiments, and while the standard errors vary appreciably, there appear to be no consistent differences between the high- and low-grade flours.

It is also pertinent to consider the recoveries and standard errors for the different levels of bromate. A selection of these follows:

Bromate, p.p.m.	5	10	20	30	40
Recovery, p.p.m.	5.1	9.7	19.6	28.9	39.5
Standard error, p.p.m.	0.13	0.13	0.29	0.37	0.38
Recovery, %	100.2	97.3	97.8	96.3	98.6
Standard error, %	1.3	1.3	1.4	1.2	1.4

These data show that both the recovery and the standard error, in terms of percent, remain relatively constant over the range from 5 to 40 p.p.m.

A final experiment was undertaken to determine whether the small loss of bromate that sometimes occurs might be related to the length of time the extract is permitted to stand before clarification. The following results were obtained: zero time, 98.5% recovery; 1 hour,

98.6%; 3 hours, 99.0%; and 4 hours, 98.6%. These results show no increasing loss of bromate with time.

Discussion

The amperometric modification appears to increase the recovery and improve the reproducibility of the determination of bromate in flour. Geddes and Lehberg (2) obtained 93-97% recovery and Johnson and Alcock (5) obtained up to 95%. It is true that Howe (4) reported recoveries as high as 100%, but Rainey's (7) collaborative study of her method yielded recoveries of 95-96%; and Armstrong (1), after modifying the method, reported estimations not exceeding 95%. In our hands, the amperometric modification gives an average recovery of about 97-98%.

Data on reproducibility of the various methods are not readily quoted. However, Rainey (7) reported errors of 6-7% at levels of 20 p.p.m. and higher for the Howe method, and considerably larger errors at lower concentrations of bromate. The amperometric modification appears to improve the reproducibility appreciably. However, a decision on this point, as well as on accuracy, must await a trial in which several laboratories collaborate.

Literature Cited

1. Armstrong, A. W. The determination of potassium bromate in flour. The Analyst **77:** 460–463 (1952).
2. Geddes, W. F., and Lehberg, F. H. The quantitative determination of bromine in bromated flours. Cereal Chem. **15:** 49–58 (1938).
3. Hoffer, A., and Alcock, A. W. A rapid method for the determination of bromate in bromated flours. Cereal Chem. **23:** 66–76 (1946).
4. Howe, Marjorie. A rapid method for the determination of potassium bromate in flour. Cereal Chem. **28:** 132–135 (1951).
5. Johnson, L. R., and Alcock, A. W. A revised method for the determination of bromate in bromated flours. Cereal Chem. **25:** 266–272 (1948).
6. Knowles, G., and Lowden, G. F. Methods for detecting the end-point in the titration of iodine with thiosulfate. The Analyst **78:** 159–164 (1953).
7. Rainey, W. L. Report on potassium bromate in flour. J. Assoc. Official Agr. Chem. **37:** 395–405 (1954).

BOOK REVIEWS

Bread. The Chemistry and Nutrition of Flour and Bread, with an Introduction to Their History and Technology. By Lord Horder, Sir Charles Dodds, and T. Moran. vii + 186 pp. Constable, London, 1954. Price: 18s.

As the title of this book indicates, the technology of milling and baking is discussed very briefly in a chapter which comprises less than 15 pages. Most of the volume is devoted to the chemistry of wheat and flour and of bread and the position of bread in the English diet. The evolution of enrichment practices in England is covered at considerable length, together with arguments for and against enrichment.

In general, the text is well written, by individuals who have had large experience in the field of interest covered by their manuscript. It contains much useful general and special information, particularly in the field of nutrition, in a limited space. The historical surveys are not exhaustive in every section, to be sure. Thus one notes the omission of reference to various significant publications, such as Ashton's *History of Bread*, Harry Snyder's collection of papers entitled *Bread*, and his earlier and historically significant papers on the digestibility of various grades of flour; also Pyler's recent (1952) books on *Baking Science and Technology*. Naturally, the references to literature on milling and baking technology at the foot of Chapter 4 are confined essentially to those concerned with British practices, and thus do not cover the parallel technics followed in American flour mills and bakeshops.

With these limitations in mind, one finds the material here presented to be arranged in concise and orderly fashion, readable, and authoritative. The document is even dramatic, to the extent that it traces very graphically the efforts of the British Ministry of Foods and its advisors to adapt and modify wartime milling and bread-baking practices and formulas in England to the critical needs of that unhappy period. With bread supplying about one-fourth of the energy and protein of the British diet during World War II, its contribution to that diet and in relation to other available food was an issue of major importance. The record of how it was met is well covered in this book. Moreover, there are significant and useful conclusions, applicable to peacetime practices, to be drawn from such wartime experiences and the nutrition studies of undernourished population groups immediately following the close of hostilities.

C. H. Bailey
University of Minnesota
St. Paul, Minnesota

Yeast Technology, by John White. xvi + 431 pp. John Wiley and Sons, Inc. New York, 1954. Price $8.00.

This book supplies a long-felt need for an authoritative treatment of the technology of yeasts. The author has had many years of experience in the baker's yeast industry in England and has skilfully utilized this background, together with information from his associates in the fermentation field, in presenting the story of the modern technology of yeasts.

A large proportion of the subject matter was derived from a series of recent papers on yeast technology and fundamental studies on yeast which appeared in the *American Brewer, Journal of the Institute of Brewing*, and *Wallerstein Communications*. Other chapters deal with yeast products, active dry yeast, food and fodder yeasts, effluent disposal from yeast factories, yeast in panary fermentations, yeast osmosensitivity, and yeast genetics. Dr. C. Rainbow and Mr. A. J. Tripper contribute chapters on "Brewer's yeasts" and "Yeasts and the baking industry," respectively. The author presents in the first chapter general data on the classification and taxonomy of yeasts with notes on their industrial importance, which could well have been expanded to give more specific information on cultures of importance to the baking industry and an elaboration of their desirable functional characteristics.

The book seems to lack coherent organization, owing in large measure to the inclusion of published papers as chapters. According to the author's foreword, 19 of the 32 chapters are based on published reports. As a consequence, original work has been presented in more detail than necessary, and certain phases of yeast technology have been inadequately covered. That the technology of active dry yeast is given only one page is a typical example of this deficiency.

Although the author comments on the differences in practice between Europe and the United States, the reader should bear in mind that the technology presented in this book is based primarily on practices in England and Europe. For example, it is claimed that the sponge method of baking has largely been superseded by the straight dough process. Actually, the extent to which these processes are used in the United States is just the reverse. The baking formulas presented have little resemblance to those in use here, hence yeast action and methods of yeast testing as applied to baking technology must be appraised accordingly.

The chapter on variation of osmosensitivity with yeast growth is thought-provoking and should stimulate further work on this interesting problem.

Yeast Technology will be a valuable reference book for food technologists, brewing chemists, cereal chemists, and investigators in other fields utilizing yeasts as research tools.

Alfred S. Schultz
The Fleischmann Laboratories
Betts Avenue
Stamford, Connecticut
Robert F. Light
Standard Brands, Incorporated
595 Madison Avenue
New York 22, N.Y.

Advances in Agronomy, Vol. V., edited by A. G. Norman. x + 422 pp. Academic Press, Inc., New York. 1953. Price $8.50.

The fifth volume in this important series deals with several diverse topics which come within the broad field of interest of the agronomist. The book contains the following sections: "A Half Century of Wheat Improvement in the United States" by S. C. Salmon, O. R. Matthews, and R. W. Leukel, U.S. Department of Agriculture; "The Soil Organic Reaction" by F. E. Broadbent, Cornell University; "Progress in Agricultural Engineering" by L. W. Hurlbut, Nebraska Agricultural Experiment Station; "Chemical Weathering of Minerals in Soils" by M. L. Jackson, University of Wisconsin, and G. D. Sherman, University of Hawaii; "The Changing Pattern of Agronomy and Horticulture" compiled by R. R. McKibbin, Central Experimental Farm, Ottawa, Canada; and "Soil Management for Conservation and Productivity" by O. R. Neal, Camp Dietrich, Maryland.

The opening chapter of 150 pages by S. C. Salmon and his associates is a very complete review of wheat improvement in the United States since the beginning of the century. The production trends in the various wheat-growing areas of the country are traced and the early developments in Kansas, Nebraska, the Northern Great Plains, the Pacific Northwest, California, and the Eastern States are outlined. Cultural practices in the various wheat-growing areas are treated historically. The development of improved varieties of the various classes of wheat is presented with information on their agronomic and milling and baking properties. A special section is devoted to the objectives of wheat breeding and to the technics for measuring milling behavior and the quality of wheats for bread, pastry, and macaroni. Other sections of this chapter deal with the various diseases and insect pests of wheat and their control.

The chapter on soil organic matter by F. E. Broadbent deals with the formation, distribution, and composition of organic matter as well as with physicochemical properties and methods of determination. In the chapter on agricultural engineering, L. W. Hurlbut traces the increased use of power and other important developments during the past 50 years which have made possible a marked increase in per capita production. Part of this chapter is devoted to harvesting and storage practices for grain and hay.

The chapter on agronomic and horticultural trends in Canada, compiled by

R. R. McKibbin, contains a section on cereals by C. H. Goulden, Chief of the Cereals Division, Central Experimental Farm, Ottawa, in which the history of the development of different varieties of wheat and other cereals is traced. Recent data on the distribution of the varieties are included.

The material contributed by S. C. Salmon and his colleagues for the United States and by C. H. Goulden for Canada constitutes such a comprehensive and authoritative account of wheat and wheat improvement on the American continent that this volume should be on every cereal chemist's bookshelf.

W. F. Geddes
Department of Agricultural Biochemistry
Institute of Agriculture
University of Minnesota
Saint Paul, Minnesota

An Introduction to Bacterial Physiology. E. L. Oginsky and W. W. Umbreit. W. H. Freeman and Company: San Francisco, 1954. 416 pp. Price as text $6.00.

The authors provide an authoritative and comprehensive treatment of the subject of bacterial physiology. This accomplishment is enhanced by the fact that the contents can be readily read and understood by the undergraduate student in this and allied fields and should therefore be widely accepted as a text.

The book is divided into six sections. The first, called "The Nature of Bacterial Physiology," deals with the basis of this discipline, its scope, and sources of reference. The difference between bacterial physiology and bacterial biochemistry is emphasized. An excellent presentation of the scientific method is included which should be of special value to the neophyte. Section two is concerned with bacterial anatomy and includes methodology. The structure of the bacterial cell is discussed from the point of view of function. Section three, "Populations," consists of five chapters covering growth, nutrition, the chemical environment, the physical environment, and genetics. The seven chapters of the fourth section, entitled "Metabolism," follow the classical treatment of this subject insofar as coverage is concerned, albeit several aspects are treated in a unique and lucid manner. This is particularly true of the chapter on enzymes and the one dealing with energy. The fifth section bears the title "Variations on a Theme," and is concerned with the "self-reliants" or autotrophic bacteria and the "dependents," i.e., the viruses and rickettsia. The final section, "The Capacity of the Cell," treats adaptation, mechanisms of survival, and virulence.

The literary style, the format, and the illustrations are excellent. The questions at the end of each chapter, whereas often conventional in nature, in some cases pose provocative problems for the student. Comments on the selected bibliography are included which serve to orient the beginner. The authors take a definite stand on controversial issues, thus resolving some of the difficulties often encountered by the student. Inasmuch as bacterial metabolism is often taught as a separate course in university curricula, it might have been desirable to have reduced the space allotted to this subject (approximately one-third of the book) and have expanded somewhat in other sections, especially section three.

Herman C. Lichstein
Department of Bacteriology and Immunology
University of Minnesota
Minneapolis, Minnesota

Silage Fermentation. By A. J. G. Barnett. Academic Press Inc., New York; Butterworths Scientific Publications, London; 1954. Price $5.00.

For the American reader this book of 202 pages might more appropriately be titled *Grass Silage Fermentation* because its emphasis is placed on fermentation of grasses, legumes, kale, and similar materials, commonly referred to in this country as "grass" to distinguish them from the more common corn silage, which is dealt with only incidentally here. This matter is of small importance, however, because the book will be very useful to anyone concerned with silage of any type.

After discussing the reasons for ensiling crops and the fundamental changes that occur during ensiling, the author describes the use of additives or preservatives and various methods of ensiling, including pits, stacks, and tower silos. Experimental silage production on pilot and laboratory scales also are described, with special emphasis on types of useful information that can be obtained from laboratory experiments. Thirty pages are devoted to a discussion of losses that occur when forage is ensiled, due to plant respiration, microbial fermentation, drainage, top and side spoilage, and the like. Methods of preventing or minimizing these losses are discussed. Lactic acid formation in silage is treated in a separate chapter, followed by a discussion of the formation of lower fatty acids, amino acids, and volatile bases. Two chapters are devoted to silage analysis, one dealing with sampling and measurement of pH, dry matter, protein, crude fiber and the like, the other to measurement of carbohydrate, acids, bases, amino acids, vitamins, and minerals. Finally the digestibility and nutritive value of silage are discussed.

The book is well organized and clearly written. Analytical data, taken both from the author's work and from other literature, are liberally presented in tables and graphs. The book is well documented and has a very satisfactory index.

E. M. Foster
Department of Bacteriology
University of Wisconsin
Madison, Wisconsin

The Story of Spices. By John W. Parry. Chemical Publishing Co., Inc., New York, N. Y. 1953. viii+208 pp. Price $4.50.

This book is a fascinating and highly readable account of the origin and development of the spice trade and its powerful influence on the progress of civilization, rather than a manual listing various spices and their properties.

Through a prologue, 19 chapters, and an epilogue the origin and uses of spices in foods, medicine, religion, and as cosmetics are briefly but interestingly recounted from the time of the Sumerians 6,500 years ago up to the present period.

The intense need for spices to brighten or modify the dismal life of ancient times was such that control of the spice trade was synonymous with unbelievable wealth and power. Empires rose and fell as dominance of the spice trade passed from one to another. The tremendous costs in manpower and ships in the persistent search for new routes to the spice-producing areas are vividly described. This violent, historic struggle is contrasted with the present-day peaceful spice trade and casual acceptance of spices by the consumer.

The Appendix includes a brief nontechnical section describing the common spices and a bibliography containing 70 references. There is an index six pages in length.

This book is recommended for those desiring a historical background in the spice field. The contents are of general interest, however, and provide fascinating reading.

C. W. Bice
The R. T. French Company
Rochester 9, New York

General Chemistry. By Linus Pauling. Second edition, xii + 710 pp., 193 figs., 2 plates. W. H. Freeman and Co., San Francisco, 1953. Price $6.00.

In the preface to the second edition of this well known text on *General Chemistry*, Pauling points out that the present edition has been written "in such a way as to make it especially suited to use by first-year college students who plan to major in chemistry and by other well-prepared students with a special interest in the subject." After emphasizing the difficult situation which faces university and college teachers of chemistry because of the great increase in chemical knowledge during the last fifty years, the author goes on to say: "The introduction of new general principles through the development of theoretical chemistry has made it possible to leave out some of the material formerly included in the first-year course. In particular, a smaller amount of time can now be devoted to learning the facts of descriptive chemistry, because many of these facts have been correlated and

systematized by new principles. Some of the nonmathematical parts of modern science, especially the descriptive aspects of atomic and molecular structure, can then be introduced during the first year. A part of elementary physical chemistry can also be treated during the first year, leaving time in later years for more advanced parts of this subject to be discussed. Some of these topics may be discussed with such thoroughness in the general chemistry course that they need not be taken up again in later courses, except for review or for amplification by more mathematical treatment."

The second edition is based on this plan and the order in which the various topics are presented permits a straightforward development of the subject. Three new chapters, two dealing with atomic physics and one with biochemistry, have been introduced and many of the other chapters which appeared in the first edition published in 1947 have been extensively revised. The new chapters on atomic physics contain a discussion of the discovery of X-rays, radioactivity, the electron, the atomic nucleus, the quantum theory, the Bohr theory of the atom, and other aspects of atomic science. In the chapter on biochemistry, the structure and properties of proteins, enzymes and their action, vitamins and hormones, chemistry and medicine, and the relation between molecular structure and physiological activity are discussed.

This book clearly shows the close relation between chemistry, mathematics, and physics. Also some philosophy of science is presented throughout the text. While written primarily as a text for first-year college students majoring in chemistry, it should be on the book-shelf of every chemist and biochemist.

W. F. Geddes
Professor of Agricultural Biochemistry
University of Minnesota
Saint Paul 1, Minnesota

Laboratory Instruments—Their Design and Application. By A. Elliott and J. Horne Dickson. 414 pp. Chemical Publishing Company, Inc., New York, 1953. Price $7.50.

The subject matter indicated by the title is extremely broad and complex and the authors have made a broad general coverage of a number of phases of this subject with the result, not uncommon in books of this nature, that some phases are not given comprehensive treatment. The authors state that no attempt has been made to cover the entire field of instrument design but rather to show the interrelation of good design, materials, and methods of construction.

The first five chapters deal with properties of materials used for general construction of instruments, the accuracy attainable in machining operations, observations on casting and jointing of metals, and preparation of drawings. These make for interesting reading and a better understanding of a designer's problems, but do not contain sufficiently detailed information to serve as a basis for design by the reader.

Chapters on constrained motion and restraints, the magnification of small displacements, sensitivity and errors of instruments, and isolation of apparatus from disturbing influences and damping are well written and the information given in these chapters should, when applied, result in greater accuracy from and more ease of operation of a great many laboratory instruments.

Chapter 11 contains a brief discussion of tests for straightness, flatness, and squareness with an indication of some of the limitations of each method.

Chapters 12 and 13 cover glass and the working of glass, and although interesting are too brief to provide an adequate working knowledge.

Chapters 14 and 15 are on lenses, mirrors, and prisms and on optical instruments. These chapters reflect the authors' main interest and are the most comprehensive of the book. The general application of lenses, mirrors, and prisms to research problems is discussed.

The 16th and final chapter contains a short outline on the use of photography in research. There is a brief discussion of film emulsions, characteristic curves, exposure, grain, resolution, processing, light sources, filters, shutters, and lenses.

The book is well indexed and the bibliographies following each chapter are

reasonably adequate though most of the references are to British sources which are inaccessible to all but those with extensive library facilities.

The book may be a useful addition to larger industrial and academic research libraries, but will probably not be of more than general interest to the majority of the readers of this JOURNAL.

C. W. OFFELT
Northern Utilization Research Branch
Peoria, Illinois

Starch and Its Derivatives. By J. A. Radley. Third Edition. Volume I, xi + 510 pp.; Volume II, xi + 465 pp. John Wiley & Sons, Inc., New York, 1954. Price, $10.00 per volume.

The third edition of *Starch and Its Derivatives* appears in two volumes instead of the one volume text of previous editions. This change has been made necessary by the increased scope of the subject matter, largely the result of rapid expansion in starch chemistry and technology research since the second edition was published, in 1943. One also notes that the number of contributors to the third edition is materially larger, compared to earlier editions. Authorship is now more international in complexion; several well known American workers in the field have contributed chapters on phases of starch research with which they have been identified.

The first volume is largely devoted to the fundamental subjects of the structure of starch molecules and their chemical and physical properties. The occurrence of starch in nature, its synthesis and amylolysis in plant processes, and its interrelationship with sucrose is ably presented by Stanley Peat under the heading, Biological Function of Starch. L. Hough and J. K. N. Jones have thoroughly revised the chapter dealing with the chemical structure of starch, originally written for the second edition by E. L. Hirst. After a discussion by Radley of some of the important physical properties of starch, particularly gelatinization, the subject of starch fractionation is reviewed by T. J. Schoch. This excellent dissertation is probably more complete and extensive than any which has appeared heretofore on this subject. There are 437 literature references for this chapter. Minor, non-carbohydrate, constituents of starch and the well known starch-iodine reaction are discussed by Radley. The phenomenon of retrogradation is elaborated by R. L. Whistler. A highly illuminating and comprehensive discussion of the waxy cereals and starches is presented by Hixon and Brimhall, which alone is worth the price of the volume. This chapter is the most comprehensive account of the botany, genetics, and agronomy, as well as the chemistry of these materials that has appeared in print up to this writing. Preliminary to a presentation of the orthodox reactions entered into by starch, written under several chapter headings by E. F. Degering, Radley, and G. V. Caesar, is a discussion by the latter of the significance of the hydrogen bond in starch. The latter portion of the first volume is devoted to a review of amylases and their action, by Radley.

Volume II of this work is comprised of three sections. The first deals with the manufacture of starch from various sources and the production of starch products including not only dextrins and physical modifications, but also glucose (dextrose), starch sirups, and chemicals by fermentation processes. New contributors to this section of the third edition are R. W. Kerr (corn starch manufacture) and Christensen and Underkoffler (fermentation chemicals).

The industrial applications of starch and starch products are reviewed in the second section. These include the use of starch and dextrins as adhesives and the application of starch products in the foodstuffs, paper, and textile industries as well as miscellaneous uses. In addition, the highly important subject of the role of starch in bread staling is very ably summarized and presented by C. W. Bice and W. F. Geddes.

The closing section is devoted to the analysis and examination of starch. A very welcome addition to this section in the third edition is an extensive discussion of methods and equipment used to determine the rheological properties of starch pastes, sols, and gels. This is presented by Kesler and Bechtel under the chapter heading, Physical Methods of Characterizing Starch.

The appendix to the second volume contains the usual photomicrographs of starch granules and an interesting note on the significance of patent references, by C. Paine.

The two volumes are satisfactorily indexed and each is provided with its own author and subject indices. Both volumes are very well produced in clear, readable type. The photographic reproductions with which the work is profusely illustrated are printed on high quality coated paper and are exceptionally clear.

The volumes are conservatively priced considering their size, the technical nature of the subject matter and the present high cost of publication.

Among the few criticisms which could be listed, the most important perhaps is the apparent length of time which has transpired between writing of the text by the several authors and publication. Many of the chapters contain references to the literature no later than about 1948–9. Five years is a comparatively long period of time in a field as active and progressive as starch chemistry. References later than 1950 in other chapters are insignificant in number and none could be found later than 1951. Although this delay was quite beyond the control of the editor, and was the result of postwar economic and political conditions, as intimated in the preface to the third edition, the result is none the less unfortunate, that this worthwhile addition to starch literature was not made available to workers in the field at a time when its usefulness would have been at the highest level.

RALPH W. KERR
George M. Moffett Research Laboratories
Argo, Illinois

ERRATUM

Cereal Chemistry, Vol. 31, No. 5

(September, 1954)

PAGE 430, Watson and Hirata.

Figure 1 is reversed and unlettered. Please substitute the illustration below.

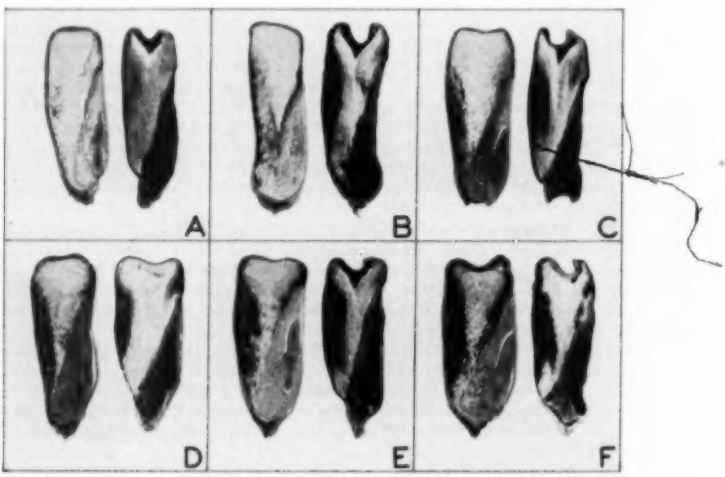


Fig. 1. Longitudinal sections and surfaces of corn kernels representing different degrees of steeping. The left figure in each pair is the brushed, 40μ section stained with I₂-KI; right figure is a cut surface to show horny (dark areas) and floury endosperm (lighter areas). Germ areas are on the right side of each kernel. Dark areas at the crown are holes. Scores are given in Table IV.

Cereal Chemistry

EDITORIAL POLICY

Cereal Chemistry publishes scientific papers dealing with raw materials, processes, or products of the cereal industries, or with analytical procedures, technological tests, or fundamental research, related thereto. Papers must be based on original investigations, not previously described elsewhere, which make a definite contribution to existing knowledge.

Cereal Chemistry gives preference to suitable papers presented at the Annual Meeting of the American Association of Cereal Chemists, or submitted directly by members of the Association. When space permits, papers are accepted from other scientists throughout the world.

The papers must be written in English and must be clear, concise, and styled for **Cereal Chemistry.**

Manuscripts for publication should be sent to the Editor in Chief. Advertising rates may be secured from and subscriptions placed with the Managing Editor, University Farm, St. Paul 1, Minnesota. Subscription rates, $11.00 per year. Foreign postage, 50 cents extra. Single copies, $2.50; foreign, $2.60. Back issues, $3.00.

SUGGESTIONS TO AUTHORS

General. Authors will find the last volume of *Cereal Chemistry* a useful guide to acceptable arrangements and styling of papers. "On Writing Scientific Papers for Cereal Chemistry" (*Trans. Am. Assoc. Cereal Chem.* 6:1–22. 1948) amplifies the following notes.

Authors should submit two copies of the manuscript, typed double spaced with wide margins on 8½ by 11 inch white paper, and all original drawings or photographs for figures. If possible, one set of photographs of figures should also be submitted. Originals can then be held to prevent damage, and the photographs can be sent to reviewers.

Titles and Footnotes. Titles should be specific, but should be kept short by deleting unnecessary words. The title footnote shows "Manuscript received . . ." and the name and address of the author's institution. Author footnotes, showing position and connections, are desirable although not obligatory.

Abstract. A concise abstract of about 200 words follows title and authors. It should state the principal results and conclusions, and should contain, largely by inference, adequate information on the scope and design of the investigation.

Literature. In general, only recent papers need be listed, and these can often be cited more advantageously throughout the text than in the introduction. Long introductory reviews should be avoided, especially when a recent review in another paper or in a monograph can be cited instead.

References are arranged and numbered in alphabetical order of authors' names and show author, title, journal, volume, first and last pages, and year. The list is given at the end of the paper. Reference numbers must invariably be cited in the text, but authors' names and year may be cited also. Abbreviations for the names of journals follow the list given in *Chemical Abstracts* **45:** VII–CCLV (1951).

Tables. Data should be arranged to facilitate the comparisons readers must make. Tables should be kept small by breaking up large ones if this is feasible. Only about eight columns of tabular matter can be printed across the page. Authors should omit all unessential data such as laboratory numbers, columns of data that show no significant variation, and any data not discussed in the text. A text reference can frequently be substituted for columns containing only a few data. The number of significant figures should be minimized. Box and side headings should be kept short by abbreviating freely; unorthodox abbreviations may be explained in footnotes, but unnecessary footnotes should be avoided. Leader tables without a number, main heading, or ruled lines are often useful for small groups of data.

Tables should be typed on separate pages at the end of the manuscript, and their position should be indicated to the printer by typing "(TABLE I)" in the appropriate place between lines of the text. (Figures are treated in the same way.)

Figures. If possible, all line drawings should be made by a competent draftsman. Traditional layouts should be followed: the horizontal axis should be used for the independent variable; curves should be drawn heaviest, axes or frame intermediate, and the grid lines lightest; and experimental points should be shown. Labels are preferable to legends. Authors should avoid identification in cut-lines to be printed below the figure, especially if symbols are used that cannot readily be set in type.

All drawings should be made about two to three times eventual reduced size with India ink on white paper, tracing linen, or *blue*-lined graph paper; with any other color, the unsightly mass of small grid lines is reproduced in the cut. Lettering should be done with a guide using India ink; and letters should be 1/16 to 1/8 inch high after reduction.

All original figures should be submitted with one set of photographic reproductions for reviewers, and each item should be identified by lightly writing number, author, and title on the back. Cut-lines (legends) should be typed on a separate sheet at the end of the manuscript. "Preparation of Illustrations and Tables" (*Trans. Am. Assoc. Cereal Chem.* **3**: 69–104. 1945) amplifies these notes.

Text. Clarity and conciseness are the prime essentials of a good scientific style. Proper grouping of related information and thoughts within paragraphs, selection of logical sequences for paragraphs and for sentences within paragraphs, and a skillful use of headings and topic sentences are the greatest aids to clarity. Clear phrasing is simplified by writing short sentences, using direct statements and active verbs, and preferring the concrete to the abstract, the specific to the general, and the definite to the vague. Trite circumlocutions and useless modifiers are the main causes of verbosity; they should be removed by repeated editing of drafts.

Editorial Style. A.A.C.C. publications are edited in accordance with *A Manual of Style*, University of Chicago Press, and *Webster's Dictionary*. A few points which authors often treat wrongly are listed below:

Use names, not formulas, for text references to chemical compounds. Use plural verbs with quantities (6.9 g. were). Figures are used before unit abbreviations (3 ml.), and % rather than "per cent" is used following figures. All units are abbreviated and followed by periods, except units of time, which are spelled out. Repeat the degree sign (5°–10°C.). Place 0 before the decimal point for correlation coefficients ($r = 0.95$). Use * to mark statistics that exceed the 5% level and ** for those that exceed the 1% level; footnotes explaining this convention are no longer required. Type fractions on one line if possible, e.g., $A/(B + C)$. Use lower case for farinograph, mixogram, etc., unless used with a proper name, i.e., Brabender Farinograph. When in doubt about a point that occurs frequently, consult the Style Manual or the Dictionary.

The NEW Precision STERWIN FEEDER for dry powders

There's easy, accurate, trouble-free feeding of dry milling materials every time you set the feed-rate knob and throw the switch on the new Sterwin Feeder.

For the feed rate is controlled by a precise micrometer adjustment, assuring unprecedented accuracy and uniformity and requiring a minimum of operator's attention.

Precision-engineered specifically for the milling and feed industries, the Sterwin Feeder provides exact feeding of Vextram®, Oxylite®, Bromate mixtures, Malt, and other dry powders.

FEATURES OF THE STERWIN FEEDER

1. Transparent front door allows full view of operation.
2. Feed rates obtained by single adjustment knob.
3. Range: 4 oz. to 5 lbs. per hour at low speed, 3 lbs. to 60 lbs. at high speed. Special, easily changed gears for higher rates.
4. Floor space only 22" x 27" . . . height 27".
5. Transparent lid gives complete view of contents.

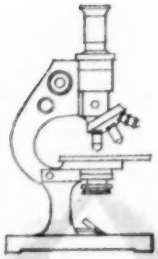
Low power requirements and simplicity of design make the Sterwin Feeder extremely economical to operate and maintain. And extreme uniformity of feeding reduces the overage ordinarily required to take care of feed-rate variations.

For complete information on the new Precision Sterwin Feeder . . . ask your Sterwin Technically Trained Representative or write:

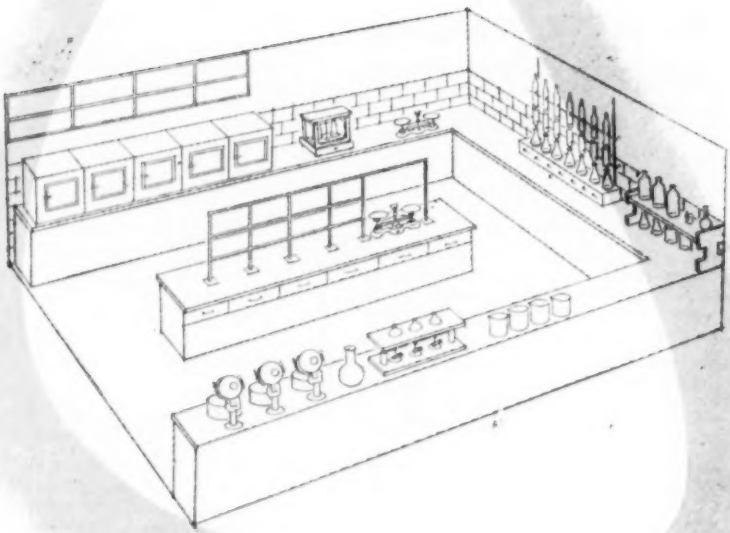
Sterwin Chemicals Inc.
Subsidiary of Sterling Drug Inc.
Flour Service Division
1133-25 MERRIAM BLVD., KANSAS CITY, KANSAS
SPECIALISTS IN FLOUR MATURING, BLEACHING AND ENRICHMENT

IN CANADA:
Sterwin Chemicals of Canada, Ltd.
1019 Elliott Street W., Windsor, Ont.

In Fleischmann's new laboratory



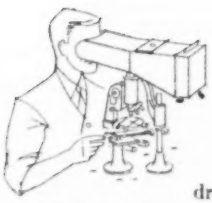
there's a



room so small

it's cleaned with a

"micromanipulator"



ON A SLIDE, one inch long, 24 private rooms are neatly arranged . . . actually each "room" is a small drop of yeast nutrient. A technician places a yeast cell measuring 1/4000 of an inch in each room. Then a search for foreign matter is made in the rooms with the aid of a high-powered microscope. All impurities are immediately removed with "micromanipulators," tiny tools which can reach into the private rooms.

This miracle of good housekeeping is but one example of the precision and painstaking care taken at the new Fleischmann's Laboratories, where new techniques are constantly being developed and improved upon to make a stronger, healthier yeast.

It is this application of science in the quality control of Fleischmann Yeast that assures you these Fleischmann benefits:

Uniformity. Every batch of yeast is exactly the same. That means tomorrow's bread will be as good as today's.

Balanced Fermentation. Controlled gas production assures proper dough conditioning . . . a fine loaf of bread every time.

Freshness. You can be sure that all its fine fermentation qualities are ready to go to work instantly.

Purity. Because it's uncontaminated from foreign wild strains and undesirable bacteria, you're assured normal healthy fermentation.

FLEISCHMANN'S YEAST

Member

FERMENTATION

IS OUR BUSINESS

AEROSOL

Larvacide®

CHLORPICRIN

50 lb. Aerosol Larvacide Cylinder with Type A Larvasoler.

The newest development for space fumigation!

Contents: 50% LARVACIDE and 50% methyl chloride (liquefied gas)

Cylinders: 50, 100, 150 and 250 lbs. net

- Easy Application – Just Open Valve!
- Fast Airing – No Liquid Touches Floor!
- Short Exposure Time – Quick Kills!
- Safer Because of Tear Gas Warning!

Write today for the new "GUIDE TO EFFECTIVE AND SAFER MILL FUMIGATION WITH LARVACIDE AND AEROSOL LARVACIDE."

Larvacide Products, Inc.

117 Liberty Street, New York 6, N. Y.
West Coast Office: 1515 Third Street, San Francisco 7, Calif.

STORAGE

OF CEREAL GRAINS AND THEIR PRODUCTS

J. A. Anderson
A. W. Alcock
editors

1954 • 6 x 9 • x + 515 pp. • 90 illustrations, 52 tables
1120 references

Price: $11.00

AMERICAN ASSOCIATION OF CEREAL CHEMISTS

University Farm St. Paul 1, Minnesota

The greatest improvement in leavening agents in years... PY-RAN

FACT 1: **What PY-RAN* does for you** . . . gives leavening *stability* never before possible.

FACT 2: **Composition of PY-RAN** . . . this compound is a new, coated, anhydrous monocalcium phosphate leavening agent just put on the market by Monsanto.

FACT 3: **How coating helps** . . . each granule of PY-RAN has moisture-absorbent covering which protects it against premature reaction during storage.

FACT 4: **Stability's effect on shelf-life** . . . aging tests conclusively prove PY-RAN's superior stability increases the life of prepared mixes and self-rising flour.

FACT 5: **Stability's effect on CO_2 release** . . . greater stability of PY-RAN assures a controlled release of gas, even after long storage. Tests clearly prove PY-RAN releases less CO_2 during first two minutes of mixing of dough or batter. *More CO_2 is available for release during oven baking.*

FACT 6: **Other PY-RAN advantages** . . . slow, controlled release of gas, as produced by PY-RAN, gives excellent texture and volume, plus good crust and crumb color. Tunneling is virtually eliminated.

FACT 7: **Blending** . . . PY-RAN will blend perfectly with other leavening phosphates such as Monsanto SAPP and HT phosphates. Monsanto's completely equipped food laboratory will show you the best methods.

FACT 8: **Information** . . . to get accurate, authentic information on PY-RAN or copy of new booklet, "MONSANTO PHOSPHATE LEAVENING AGENTS," write to MONSANTO CHEMICAL COMPANY, Inorganic Chemicals Division, 1700 South Second Street, St. Louis 4, Missouri.

*Reg. U. S. Pat. Off.

Other Members of Monsanto's Leavening Family

MONSANTO SAPP-40
ideal for machine doughnut mixes

MONSANTO SAPP-28
a slow-action baking acid

MONSANTO HT* Phosphate . . .
MCP monohydrate: use it alone or with other mixes for results.

MONSANTO
CHEMICALS—PLASTICS

SERVING INDUSTRY . . .
WHICH SERVES
MANKIND

BAKING
SCIENCE AND TECHNOLOGY

By E. J. Pyler,
Editor, The Bakers Digest,
in collaboration with the
staff and faculty of the
Siebel Institute of Technology

This is the first reference work to be published on this subject in almost 20 years. It covers just about every conceivable phase relating to modern bakery production. It's indexed for quick, easy reference.

CONTENTS

In Two Volumes — Over 800 pages

I. The scientific facts on carbohydrates, fats and oils, proteins, enzymes, vitamins, micro-organisms and physical chemistry.

II. Detailed information about wheat and miscellaneous flours, sugars and syrups, shortenings, milk products, egg products, water and salt.

III. Thorough discussion of the modern principles of dough mixing, fermentation, make-up, baking, rye bread production, bread-staling, and testing methods.

IV. Cake baking, with details on ingredients, flavor, techniques, and miscellaneous bakery products.

V. Bakery equipment, including flour handling units, mixers, dividers, rounders, moulders, ovens, bread coolers, slicers and wrappers, etc., and bakery sanitation.

PRICE: $15.00, Two Volumes

REVIEWS AND COMMENT

Journal of the A.O.A.C.:
". . . a good source of reference for the bakery production man, baking chemist, cereal chemist . . ."

Food Technology:
"The author will long be remembered in the baking industry for the monumental task he has done in assembling a vast amount of material in a form which makes it so useful a book to so many in all phases of the baking industry."

Cereal Chemistry:
"The volumes will be valued additions to any reference library."

C. H. Bailey,
University of Minnesota:
"These are truly magnificent documents."

C. W. Brabender:
"May I congratulate you for this excellent piece of work which is really a great contribution to the further development of the baking industry."

A Recomended Text at:
Florida State University
Kansas State College
University of Wisconsin

SIEBEL PUBLISHING Company, Dept CC1, 4049 Peterson Ave., Chicago 30

Please send me_____copies of "Baking Science and Technology," at $15.00 per two volume set.

Check Enclosed (Postage Prepaid)

Send C.O.D. ($15.00 per set, plus mailing charges)

NAME_____

Address_____

City_____ Zone_____ State_____

SHORTENINGS YOU CAN DEPEND UPON

PRIMEX B&C

An all-hydrogenated vegetable oil shortening of exceptional stability. Excellent for all deep frying purposes. Preferred by biscuit and cracker bakers, manufacturers of prepared biscuit, pie crust and doughnut flours, and makers of other food products where rancidity troubles are to be avoided.

SWEETEX

The "High-Ratio" shortening. Especially designed to permit bakers to produce "High-Ratio" cakes, icings, and sweet yeast goods with superior eating and keeping qualities.

NUTEX

An all-hydrogenated vegetable oil shortening combining the exceptional stability of Primex B&C and the "High-Ratio" properties of Sweetex. A top quality shortening manufactured for use in prepared cake, yeast raised doughnuts and sweet yeast dough, and icing mixes.

PRIMEX

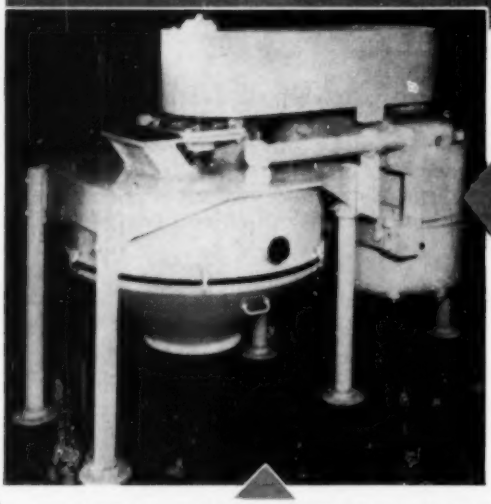
The all-hydrogenated shortening "that sets the quality standard." A top grade shortening especially recommended for doughnut frying, for pies, cookies and bread, and for other shortening purposes.

PROCTER & GAMBLE

Branches and warehouses in principal cities

General Offices . . . . . CINCINNATI, OHIO

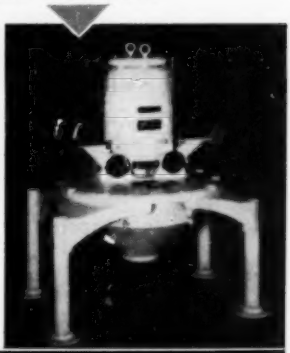
500 CWT PER HOUR!!!
it's a cinch with the NEW "BIG INCH"....



for Positive Infestation Control . . .

the NEW "ENTOLETER" 'BIG INCH' for 150 to 500 cwt per hour

the STANDARD "ENTOLETER" unit for 25 to 150 CWT per hour



You guarantee your flour specifications... let "ENTOLETER" Infestation Control assure the complete cleanliness of all ingredients and finished products . . .

. . . the trademark "ENTOLETER" on milling equipment is your guarantee of complete satisfaction. Write to us for information concerning our products. ENTOLETER DIVISION, The Safety Car Heating and Lighting Company, Inc., 1153 Dixwell Ave., New Haven 4, Connecticut.

The trademark "ENTOLETER" is your guarantee of complete satisfaction

ENTOLETER
CENTRIFUGAL MACHINES

STRENGTHEN YOUR POSITION....

WITH

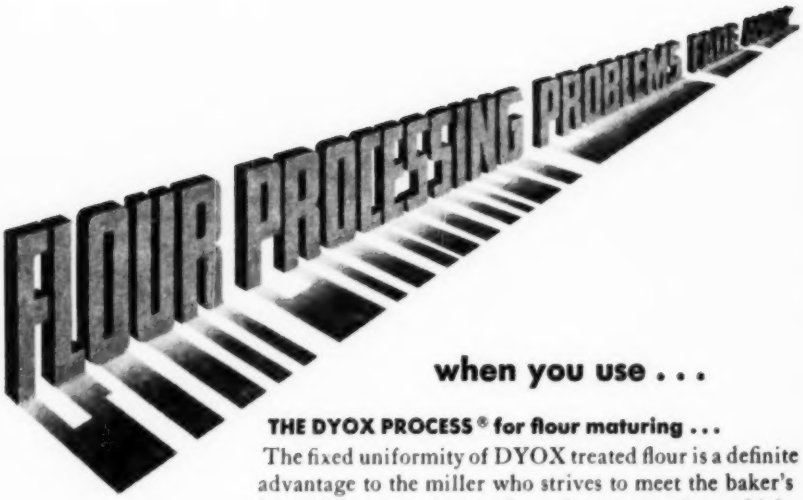
Paniplus

THE DOUGH CONDITIONER

TABLE FRESHNESS BEGINS AT THE MIXER!

Here Paniplus assures proper gluten development and maximum gluten hydration. This means improved Natural Moisture Retention in your bread and rolls — a strong move towards increased sales and reduced stale.

THE PANIPLUS COMPANY • 742 BOARD OF TRADE BUILDING • KANSAS CITY 6, MISSOURI



when you use . . .

THE DYOX PROCESS® for flour maturing . . .

The fixed uniformity of DYOX treated flour is a definite advantage to the miller who strives to meet the baker's demand for a starting product of constant value—which works in the bake shops with the least trouble and manipulation by the operator. DYOX treated flour assures overall dependability, uniformity of product, and ease of operation.

"NOVADELOX"® for whiter, brighter flour . . .

"Novadelox" is designed to meet the desire of the consuming public for a bread that is truly white—and to enable millers to produce a uniform product of standard color.

"N-RICHMENT-A"® for uniform enriching . . .

"N-Richment-A" provides a readily available, simple and troublefree product for enriching flour—with the assurance that the standard procedure of adding "N-RICHMENT-A" will produce a dependable standardized flour.

THE N-A FLOUR SERVICE DIVISION with more than a quarter-century of experience . . .

The N-A Flour Service Division with its skilled laboratories and staff is always available to work with you or your consultants on all phases of maturing, bleaching and enriching. Why not phone your nearest N-A Representative today!

DYOX
for flour maturing

NOVADELOX
for a whiter, brighter flour

N-Richment-A
for uniform enrichment

NA-62

NOVADEL FLOUR SERVICE DIVISION

WALLACE & TIERNAN INCORPORATED

BELLEVILLE 9, NEW JERSEY

REPRESENTATIVES IN PRINCIPAL CITIES